UNIVERSITY OF ALBERTA

Advanced Oxidation Treatment of Aged Raw and Biologically Treated Landfill Leachates

By

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DEDICATION

This work is dedicated to my family members who love me and support me during my whole journey of education.

My mother and my father always believe that I can succeed in my education. Without their trust, I would have chosen a college when I graduated from Junior High School. When I have opportunities to look at the large cities and most parts of the world, I really appreciate my parents' trust.

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ABSTRACT

Ozone only (O_3 only), ozone with hydrogen peroxide (O_3/H_2O_2), and hydrogen peroxide with ultraviolet radiation (H_2O_2/UV) were applied to the aged raw leachate and the membrane fractionated aged raw leachates. In addition, O_3 only was also applied to the landfill leachate after treatment with rotating biological contactor (RBC effluent).

Regression models of COD, ratio of BOD_5/COD, NH_3-N, and alkalinity as functions of used-ozone dose were developed for the aged raw leachate after O_3 only and O_3/H_2O_2 treatments. At a 95% confidence level, no significant difference was found in COD, ratio of BOD_5/COD, NH_3-N, and alkalinity of O_3 only and O_3/H_2O_2 treatments. Carbon mass balance on the ozonation of the aged raw leachate showed a good agreement between the carbon captured in the off-gas during ozonation and the calculated carbon loss due to alkalinity reduction and organic compound oxidation. There was also a good agreement between the carbon captured in the off-gas of ozonation and the total carbon loss after ozonation as well. Mass distribution profiles of COD, BOD_5, colour and metals of the aged raw leachate were developed between the aged raw leachate and the membrane fractionated aged raw leachates. Some metal species in the aged raw leachate were associated with the large organic molecules. UV fluence was the most significant factor for COD and colour reduction and BOD_5 improvement for the aged raw leachate during H_2O_2/UV treatment.

No correlation was observed between BOD_5 increase and formation of new peaks for O_3 only, O_3/H_2O_2, and H_2O_2/UV by means of molecular size distribution analysis. The relationships of used-ozone dose, COD, BOD_5, ratio of BOD_5/COD as functions of the total peak area of the molecular size distribution with O_3 only treatment were

developed for the aged raw leachate and the RBC effluent. The regression model of BOD_5 after oxidation with O_3 only as a function of total peak area of the molecular size distribution was also developed for the membrane fractionated aged raw leachates. Molecular size distribution demonstrated clearly that the particles in the samples hindered the reduction of the large molecule peaks in the H_2O_2/UV process.

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ABBREVIATIONS AND NOMENCLATURES

Ag_2SO_4: Silver sulphate;

ARL: Aged raw leachate;

AUFS: Absorbance unit full scale;

BOD: Biochemical oxygen demand, mg/L;

BOD_5/COD: ratio of five-day biochemical oxygen demand to chemical oxygen demand;

BOD_5: Five-day biochemical oxygen demand, mg/L;

$Ca(OH)_2$: Calcium hydroxide;

$CaCO_3$: Calcium carbonate;

CBLLTP: Clover Bar Landfill Leachate Treatment Plant;

CBSL: Clover Bar sanitary landfill;

CO_2: Carbon dioxide;

COD: Potassium dichromate chemical oxygen demand, mg/L;

COD_{Mn}: Chemical oxygen demand determined with potassium permanganate, mg/L;

DO: Dissolved oxygen, mg/L;

DOC: Dissolved organic carbon, mg/L;

°Hasen: Colour unit, equals to Pt-Co colour unit;

H_2O_2/Fe^{2+}/UV: Photo Fenton process or photo-assisted Fenton process;

H_2O_2/Fe^{2+}: Fenton process;

H_2O_2/UV: Hydrogen peroxide combined with ultraviolet radiation;

H_2O_2: hydrogen peroxide;

H_2SO_4: Sulphuric acid;

HCO_3^-: Bicarbonate;

HPLC: High performance liquid chromatograph;

i: Order number;

ICP/MS: Inductively coupled plasma/mass spectroscopy;

IR: Infrared ray;

$K_2Cr_2O_7$: Potassium dichromate;

KI: Potassium iodide;

MFARL: Membrane fractionated aged raw leachate;

MW: Molecular weight;

MWCO: Molecular weight cut-off;

$Na_2S_2O_3$: Sodium thiosulfate;

NaCl: Sodium chloride;

NH_3: Ammonia;

NH_3-N: Ammonia nitrogen, mg/L as nitrogen;

NMR: Nuclear magnetic resonance;

NMWL: Nominal molecular weight limit;

NO_3^-: Nitrate;

NORMSINV (*P*): Normal score;

•OH: Hydroxyl radical;

O_3/H_2O_2: Ozone combined with hydrogen peroxide;

O_3/UV: Ozone combined with ultraviolet radiation;

O_3: Ozone;

P: Probability;

PEG: Polyethylene glycol;

PVDF: Polyvinylidene fluoride;

RBC: Rotating biological contactor;

SS: Suspended solids;

TC: Total carbon, mg/L as carbon;

TCU: Two colour unit or Platinum-Cobalt colour unit (Pt-Co colour unit);

TKN: Total Kjieldahl nitrogen, mg/L as nitrogen;

TOC: Total organic carbon, mg/L as carbon;

TOX: Total organic halides;

UV: Ultraviolet radiation;

VOC: Volatile organic compounds.

CHAPTER 1 BACKGROUND INFORMATION AND RESEARCH OBJECTIVES

1.1 Clover Bar Sanitary Landfill

Clover Bar Sanitary Landfill (CBSL) is located on the southern bank of the North Saskatchewan River, east of the City of Edmonton. Its western boundary is Meridian Street (1st Street), and southern boundary is 137Avenue. The City of Edmonton has operated its CBSL since 1975. The expected closure date for CBSL will be 2006 or later. (Birch et al. 1995).

As shown in Figure 1.1, CBSL is a complex solid waste processing facility, including 15 operation units (Edmonton Waste Management Centre 2002): administration and training facility, weigh-scale facility, operation centre, research/demonstration facility, concrete/asphalt recycling facility, leachate treatment plant, wetlands, co-composter, material recovery facility, dry landfill, landfill gas plant, compost curing and marketing, biosolids lagoon, landfill and site revegetation, and the engineered sanitary landfill.

1) Administration and training facility

The administration and training facility provides classroom, demonstration and theatre space for students, visiting delegations and citizens. The real-time video is linked to various processes throughout the site.

2) Weigh-scale facility

The weigh-scale facility was designed for efficient vehicle weighing and also functions as the site access control point since all vehicles entering and leaving the site must pass through this area.

Figure 1.1 Overlook of Clover Bar Sanitary Landfill Site (Edmonton Waste Management Centre 2002).

3) Operation centre

The operation centre conducts the day-to-day site operations under direct control of the City of Edmonton.

4) Research/demonstration facility

The research/demonstration facility (currently under construction) will provide the means to conduct research and to develop and test new equipment and processes for commercial application.

5) Concrete/asphalt recycling

Over 100,000 tonnes of concrete and asphalt rubble are crushed annually to

produce aggregate used as base material for new roadways. The recycling program is one of the largest and most successful in Canada.

6) Leachate treatment plant

The landfill leachate treatment plant cost $4.4 million in 1996 and is capable of processing approximately 10 million litres of landfill leachate per year. It is one of the most sophisticated leachate treatment plants in Canada, incorporating physical, chemical and biological treatment processes.

7) Wetlands

The wetlands is a five-hectare lake. It collects surface run-off and serves as a natural bird and small wildlife habitat. The site revegetation plan will eventually link the wetlands with nearby riverbank and adjacent forested areas, and forms a unique integration of natural habitat and urban waste management.

8) Co-composter

The co-composter is the largest unit of its type in North America. It has capacity of 200,000 tonnes of municipal solid waste per year and 100,000 tonnes of dewatered biosolids (22,500 dry tonnes) per year. It produces 125,000 tonnes of compost per year. The enclosed plant area is 38,690 m^2. Along with recycling programs, the co-composter enables diversion of 65% of Edmonton's residential waste from landfill.

9) Material recycling facility

The material recycling facility is one of the most advanced material recycling facilities in North America. It incorporates the state-of-the-art mechanical systems and manual-sorting equipment to process recyclables collected through municipal programs.

The size of the material recycling plant is 5,945 m^2. The plant capacity on a single shift basis is 30,000 tonnes per year. Forty staff works in this plant.

10) Dry landfill

The 13-hectare dry landfill accepts only non-putrescible material, mainly the construction or demolition materials.

11) Landfill gas plant

The landfill gas plant cleans the landfill gas collected from the sanitary landfill. The cleansed landfill gas is used as complementary fuel to generate electricity at the EPCOR power plant. The electricity generated by the landfill gas can satisfy the annual needs of 4,000 homes.

12) Compost curing and marketing

The compost produced by the co-composter is cured at this site, and is mainly sold to the residents in Edmonton for the garden and lawn purpose.

13) Biosolids lagoons

The biosolids from the Gold Bar Wastewater Treatment Plant are stored and thickened in the biosolids lagoons, which have five ponds located on 45 hectares. The Edmonton composting facility uses the biosolids as part of its feedstock.

14) Landfill site revegetation

The innovative landfill site revegetation program involves the propagation and planting of native seedlings and grasses as the areas of the active sanitary landfill are completed.

15) Engineered sanitary landfill

The engineered sanitary landfill with capacity of 13.2 million tonnes solid waste

incorporates a groundwater diversion system, environmental monitoring, leachate and landfill gas recovery.

1.2 Clover Bar Landfill Leachate Treatment Plant

The development of CBSL site has proceeded east to west in two stages (Birch et al. 1995). The engineered landfill cells, constructed from 1979, have a 3-m thick compacted clay liner, and were also constructed with an integral leachate collection system. This system consists of an interconnected perimeter network of 100 mm diameter perforated PVC pipe laid at the base of the landfill. The pipes drain to sumps spaced around the base. Sloping riser pipes project upward from each sump along the interior berm of the landfill and exit above the surface ground. Leachate can be extracted from a sump by lowering a submersible pump down to its attendant riser. The base of the landfill itself gently slopes towards the northwest corner.

The Clover Bar Landfill Leachate Treatment Plant (CBLLTP) was designed to pretreat the leachate extracted from CBSL with capacity of 10,000 m^3/year (27.4 m^3/d), including the condensate from the landfill gas plant at flow rate of 260 m^3/year. Its peak flow rate is 15,000 m^3/year (41.1 m^3/d). The CBLLTP was commissioned in 1996. The leachate treatment operations are expected to continue at least 10 years after the closure date of the landfill. The design average and range of influent concentrations of full-scale RBCs in the CBLLTP and the surchargeable limit of the City of Edmonton's Sewers Use Bylaw (Birch et al.1995) are summarized in Table 1.1.

The process train of CBLLTP is shown in Figure 1.2. The process train is comprised of three treatment areas:

- Pretreatment processes;
- Biological treatment process; and
- Final clarification process.

Table 1.1 The design average and range of influent concentrations of full-scale RBCs in CBLLTP and the surchargeable limit.

Constituent	Design average	Range	Surchargeable limit
BOD_5, mg/L	7,600	50 to 29,000	300
COD, mg/L	11,300	600 to 45,000	600[a]
Suspended solids, mg/L	700	75 to 1,500	300
TKN, mg/L	600	100 to 1,000	50
Total ammonia nitrogen, mg/L	490	90 to 880	
Boron, mg/L	20	10 to 50	
Nickel, mg/L	18	0 to 175	
Zinc, mg/L	70	0 to 3,200	
Mercury, mg/L	0.15	0 to 0.42	
Thallium, mg/L	0.2	0 to 2.6	
Alkalinity, mg/L as $CaCO_3$	4,700	2,400 to 7,400	
Total dissolved solids, mg/L	12,600	4,000 to 36,500	
Acetone, mg/L	2.0	0.002 to 12.7	
2-Butanone, mg/L	4.0	0.003 to 19	

Note:

[a]Or twice the BOD_5 value, whichever is greater.

Table 1.2 summarizes the major unit process with loading and flow rate. Raw leachate extracted from various locations at the CBSL is hauled by a 13.6-m^3 capacity tanker truck to the plant and discharged into one of two equalization storage tanks. It is assumed that this truck will haul an average of three (3) loads per working day. Each equalization storage tank (6.7 m diameter, 5.0 m height) can hold leachate for four (4)

days to eight (8) days, depending on the flow rate through the plant. As one tank is filled, the contents of the other tank are being discharged through the plant.

From the equalization storage tanks, the leachate is pumped into a mixing tank that employs a Venturi based air-stripping unit to remove 90% of volatile organic compounds (VOCs) from the liquid phase into the airborne phase. The airborne VOCs are then directed to a catalytic oxidizer unit, which destroys 99% of VOCs at 350°C to 500°C using pellet aluminum substrate and platinum-based catalytic metal before the air stream is vented to the outside atmosphere. Air contact in the VOC stripper also causes the bulk of dissolved heavy metals in the leachate to precipitate out of the solution. Alum and polymer (Percol 408) are added to the leachate to cause the formation of flocs and to settle out the heavy metals in the primary clarifier. The equivalent surface-loading rate in the primary clarifier is less than 8 $m^3/m^2 \cdot d$ at peak flow rate of 41.1 m^3/d.

If the temperature of leachate is below 15°C, a heat exchanger can be used to warm the leachate because the biological treatment, especially the nitrifying bacteria, will generally be active above 16°C. The heat exchanger's capacity is 94.18 MJ/h to heat the leachate from 8°C to 20°C when the leachate flow rate is 27.4 m^3/d.

If TKN concentrations are high, the leachate can also be pumped through ammonia stripping tower. In conjunction with the ammonia-stripping tower, caustic soda is first added to the leachate to adjust the pH of leachate to 11. Carbon dioxide or sulphuric acid is then added to the leachate following ammonia stripping to lower the pH back to 7.5 again.

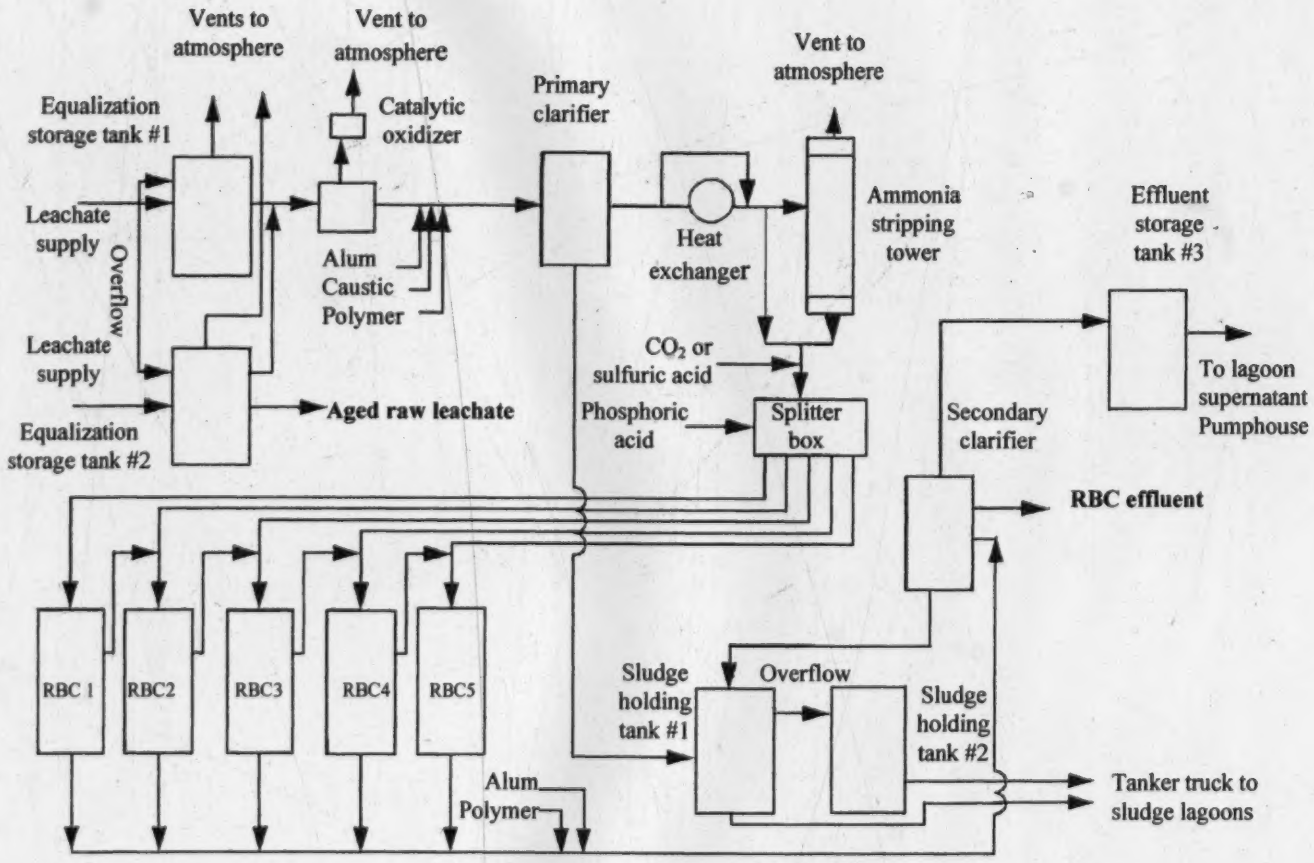

Figure 1.2 Process Train of CBLLTP (*Obtained from Waste Management Branch, the City of Edmonton).*

Table 1.2 Summary of the unit process parameters of CBLLTP (Birch et al. 1995).

Unit	Liquid storage volume m^3	Detention time, h		Comment
		Design flow 1.14 m^3/h	Maximum flow 1.71 m^3/h	
Equalization storage tank	165/tank	145	96	4 days storage per tank
Aeration for precipitation and VOC stripping	1.0	0.88	0.58	0.18 m^3/s of air to Catalytic Oxidizer
Primary clarifier	0.76	0.66	0.44	Inclined plate gravity settler
Ammonia stripping				
Tower (Packed column)		2,210 m^3/h	2,210 m^3/h	Packed tower air flow
Basin	0.86	0.75	0.5	
RBC units				5-stage 4.5 m diameter
Unit 1	80	70	47	rotors
Unit 2	80	70	47	
Unit 3	80	70	47	
Unit 4	80	70	47	
Unit 5	80	70	47	
Overall	400	350	235	
Secondary clarifier	6.75	6	4	Cone bottom gravity settler
Sludge holding tank	50			One week of sludge storage
Effluent storage tank	45	36	24	

After primary clarification or heat exchanger or/and ammonia-stripping tower, the leachate goes into a splitter box, where phosphoric acid is injected as nutrient source for rotating biological contactors (RBCs). The main purpose of the RBCs is BOD and COD reduction, with secondary consideration of the ammonia nitrogen reduction. Five units of CHEMDISK® RBCs were installed, and each unit containing 12,082 m^2 of media (CMS Group Inc.). Within the epoxy coated steel biozone tanks of RBCs, there are load cell weight monitoring, dissolved oxygen monitoring, pH monitoring, and aeration tubes inserted into each stage for air or CO_2 addition. BOD_5 loading is 5.0 $g/m^3 \cdot d$, maximum

stage 1 BOD_5 loading 15 $g/m^3 \cdot d$, TKN loading 1.5 $g/m^3 \cdot d$, BOD_5 removal efficiency 95%, and TKN removal efficiency 60%.

After RBC treatment, alum and polymer (Percol 408) are added to leachate again, and then the leachate goes to the secondary clarifier, which is a circular settling basin with perimeter weir effluent collection. The design parameters are:

- Surface overflow rate: 0.5 $m^3/ m^2 \cdot h$;
- Side water depth: 3.0 m;
- Conical bottom: 60° incline;
- Surface area (minimum): 2.30 m^2;
- Typical sludge removal concentration: 4.5%.

The final treated leachate then overflows from the secondary clarifier and into the effluent storage tank, from which it is pumped out of the plant through supernatant pumphouse and delivered to the lagoon.

The treatment sludge from both the primary and secondary clarifiers at the plant is combined in two sludge-holding tanks. As required, load of sludge are hauled away by tanker truck to the Clover Bar Sludge lagoons for interim storage.

1.3 Research objectives

The effluent from the five-stage RBC contains about 20 mg/L of BOD_5, 840 mg/L of COD, and 750 TCU of colour. Due to the pipeline modification for the RBC system, RBC system had been out of operation for one and half years. The raw landfill leachate had been stabilized in the equalization storage tank for about one year when the sample was collected. The COD, BOD_5, colour, alkalinity and pH were quite close to these

parameters of the RBC effluent. The only difference existed in the ammonia nitrogen. Since the closure date of this landfill site is very near, the characteristics of the aged raw landfill leachate could represent the characteristics of the raw leachate from the old landfills. Therefore, the aged raw landfill leachate was used for the methodology development and the experiment for the process selection. The RBC effluent was treated with the selected process to provide the design parameters for the pilot plant.

The research objectives for this project were to evaluate the impact of advanced oxidation treatment on the COD, BOD_5, ratio of BOD_5/COD (i.e., biodegradability), colour, ammonia nitrogen (NH_3-N) and alkalinity of the RBC effluent as well as the aged raw landfill leachate to such a level that it can be recycled into the RBC units, and ultimately removed by the biological processes. Specifically, the objectives are:

1. To further reduce COD and colour.
2. To improve the leachate biodegradability; i.e., BOD_5 and ratio of BOD_5/COD. Usually, the wastewater with ratio of BOD_5/COD higher than 0.1 is considered to be biodegradable, and can be recycled to the biological treatment units.
3. To investigate the changes in ammonia nitrogen and alkalinity during the advanced oxidation processes.
4. To observe the molecular size distribution before and after oxidation processes, aiming at unfolding the correlation between the oxidation by-products and BOD_5 increase after oxidation.
5. To understand the oxidation processes of O_3 only, O_3/H_2O_2, and H_2O_2/UV by taking advantage of the molecular size distribution analysis, especially the role of H_2O_2 in the combined oxidation processes.

To fulfill the research objectives mentioned above, the following investigations were carried out:

1. A complete literature research was conducted to initially select the advanced oxidation processes.
2. The aged raw landfill leachate was oxidized with ozone (O_3) only and a combination of O_3 with hydrogen peroxide (O_3/H_2O_2) at different used-ozone doses. Then a carbon mass balance was performed on the ozonation of the aged raw leachate to verify the reaction pathway of the organic compounds that were oxidized in the O_3 only process.
3. A 2^3 factorial experiment was implemented to study the impact of H_2O_2 dose, UV fluence and leachate pH on the oxidation of the aged raw landfill leachate with H_2O_2/UV. COD and colour reduction and BOD_5 increase were the measured responses.
4. The aged raw landfill leachate was fractionated with 10,000, 5,000 and 1,000 MWCO (molecular weight cut-off) membranes, and then the fractionated leachates were oxidized with O_3 only, O_3/H_2O_2, and H_2O_2/UV.
6. The RBC effluent was oxidized with O_3 only.

For all of the treatments, COD, BOD_5, colour, ammonia nitrogen and alkalinity as well as molecular size distribution before and after oxidation were observed.

1.4 References

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CHAPTER 2 APPLICATION OF ADVANCED OXIDATION METHODS FOR LANDFILL LEACHATE TREATMENT — A REVIEW [1]

2.1 Introduction

Landfill leachate is a complex wastewater generated when the moisture content or the water content of the landfilled solid waste is higher than its field capacity. The presence of water allows a combination of physical, chemical and microbial processes to transfer pollutants from the solid waste into the liquid, resulting in the formation of leachate (Christensen and Kjeldsen 1989).

Young landfill leachate contains large amount of free volatile fatty acids, resulting in high concentrations of COD, BOD, NH_3-N and alkalinity, a low oxidation-reduction potential, and black colour. Therefore, biological treatment processes are commonly employed for young landfill leachate treatment to remove the bulk biodegradable organics (Forgie 1988a).

Old landfill leachate or biologically treated young landfill leachate has a large percentage of recalcitrant organic molecules. As a result, this kind of leachate is characterized by high COD, low BOD, fairly high NH_3-N and alkalinity, low ratio of BOD/COD, a high oxidation-reduction potential, and dark brown or yellow colour. The treatment processes for this kind of leachate include chemical precipitation and coagulation (Forgie 1988b), chemical oxidation (Forgie 1988b), electrochemical oxidation (Chiang et al. 2001), reverse osmosis (Chianese et al. 1999; Linde et al. 1995;

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[1] A version of this chapter has been published. Wang F., Smith D. W. and Gamal El-Din M. 2003. *Journal of Environmental Engineering and Science*, 2(6): 413-427.

Peters 1998) and nanofiltration (Linde and Jönsson 1995; Trebouet et al. 1999; Trebouet et al. 2001; Peters 1998).

Forgie (1988b) reviewed the chemical oxidation processes for treating landfill leachates. At that time, the commonly used oxidants included chlorine, calcium hypochlorite, potassium permanganate, hydrogen peroxide, and ozone.

Hydroxyl radicals (•OH) that are highly reactive oxidizing agents are produced during advanced oxidation processes. Therefore, an advanced oxidation process is more effective than a traditional chemical oxidation process. Advanced oxidation treatment of landfill leachate using O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+}, and H_2O_2/Fe^{2+}/UV has been investigated extensively in the past decade. The primary objective of the application of these advanced oxidation processes for treating old or biologically treated landfill leachate is to oxidize the refractory organics to end-products, such as carbon dioxide and water (i.e., to reach complete mineralization), or to transform these organic substances into more easily biodegradable substances, which can be removed in a subsequent biological treatment process.

Based on previous studies, the characteristics of landfill leachates, the mechanisms of O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+}, and H_2O_2/Fe^{2+}/UV oxidation processes and their application for landfill leachate treatment are reviewed in this Chapter. In addition, the influences of NH_3-N, pH and alkalinity on the advanced oxidation processes applied for treating landfill leachates as well as the methods to remove oxidant residues are also discussed in this Chapter.

2.2 Characteristics of landfill leachates

The characteristics of the landfill leachates can usually be represented by the basic parameters COD, BOD, ratio of BOD/COD, colour, NH_3-N, pH, alkalinity, oxidation-reduction potential, and heavy metals. The values of COD, BOD, ratio of BOD/COD, pH, NH_3-N and alkalinity of young landfill leachate are much different from those of old or biologically treated landfill leachate, as shown in Tables 2.1 and 2.2.

A high moisture content or water content in the solid waste of young landfills enhances acid fermentation of the organic matters. That leads to the release of large quantities of free volatile fatty acids and causing pH to decrease. Furthermore, the lowered pH accelerates heavy metal dissolution (Chian 1977). Therefore, young landfill leachate is characterized by its high concentrations of COD and BOD, a high ratio of BOD/COD, high concentrations of NH_3-N and alkalinity, as well as a low oxidation-reduction potential. As shown in Table 2.1, BOD of young landfill leachate varies from 167 to 36,000 mg/L; COD can range from 730 to 52,000 mg/L; the range of the ratio of BOD/COD is 0.17 to 0.85; and pH can vary from 5.0 to 9.3; NH_3-N can range from 0.3 to 13,000 mg/L as N; and alkalinity varies from 560 to about 16,800 mg /L as $CaCO_3$.

The concentration of free volatile fatty acids, as well as the ratio of BOD/COD, decreases rapidly with the aging of the landfills (Chian 1977). This is due to the release of the large refractory organic molecules from the solid wastes followed by dissolution into the leachate. Consequently, old landfill leachate is characterized by its high COD, low BOD, low ratio of BOD/COD, high pH (usually pH is higher than 7.0), fairly high NH_3-N and alkalinity, and a high oxidation-reduction potential. Biologically treated young landfill leachate has similar characteristics to that of an old landfill leachate in

terms of COD, BOD, pH and alkalinity. This can be explained by the removal of major fraction of the bulk biodegradable organics in a biological treatment system and the removal of NH_3-N in the biological treatment system and/or an air-stripping unit prior to the biological treatment system. As shown in Table 2.2, for the old or biologically treated landfill leachate, BOD ranges from 1 to about 2,920 mg/L; COD varies from 207 to about 26,000 mg/L; ratio of BOD/COD varies from about 0.00 to 0.17; pH ranges from 6.8 to 9.0; NH_3-N varies from less than 5 to 3,400 mg/L; and alkalinity ranges from 1,020 to about 12,300 mg /L as $CaCO_3$.

The quality and quantity of landfill leachate vary substantially between sites and seasons, depending on such factors as type and moisture content of disposed waste; site specific hydrogeology; landfill design, operation and age of the landfill; as well as the relative biodegradability of the different organic contaminants present in the landfilled solid wastes (Reinhart and Townsend 1998). The wide range of landfill leachate characteristics leads to variable results of advanced oxidation processes when applied for landfill leachate treatment. Laboratory-scale advanced oxidation experiments using O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+}, and H_2O_2/Fe^{2+}/UV for treating landfill leachate are usually performed to select the best process for a specific landfill leachate.

Table 2.1 BOD, COD, BOD/COD, pH, NH_3-N and alkalinity of young landfill leachates.

Location of landfill	BOD, mg/L	COD, mg/L	BOD/COD	pH	NH_3-N, mg/L as N	Alkalinity, mg/L as $CaCO_3$	Reference
Canada	NA	3,210 to 9,190	NA	6.9 to 9.0	NA	NA	Kennedy and Lentz 2000
Canada	120 to 2,980	730 to 4,720	NA	6.3 to 7.8	0.3 to 427	1,350 to 3,510	Cameron and Koch 1980
Canada	13,600	19,300	0.71	5.2	NA	4,110	Zapf-Gilje and Mavinic 1981
Canada	36,000	48,000	0.75	5.02	NA	7,640	Uloth and Mavinic 1977
Canada	9,660	13,800	0.70	5.80	42	1,800	Henry et al. 1987
	1,100	3,750	0.30	6.35	36	880	
	930	1,870	0.50	6.58	10	1,070	
Canada	627	1,710	0.37	6.85	NA	1,130	Henry et al. 1983
Canada	NA	1,320 to 3,850	0.49 to 0.52	6.42 to 7.37	NA	560 to 1,650	Henry et al. 1982
Canada	1,200 to 2,700	1,800 to 4,200	0.48 to 0.85	6.6 to 7.8	NA	800 to 1,200	Muthukrishnan and Atwater 1985
Canada[a]	NA	881	NA	7.0	NA	3,740	Hausler et al. 1995
	240	740	0.32	NA	NA	NA	
Mainland, China	1,900 to 3,180	3,700 to 8,890	0.25 to 0.36	7.4 to 8.5	630 to 1,800	NA	Wang and Shen 2000
Germany	1,060	3,180	0.33	NA	884	NA	Baumgarten and Seyfried 1996
France	NA	1,930	NA	7.21	295	NA	Gourdon et al. 1989
France[b]	17,000	48,000	0.35	6.0	1,620	NA	Millot et al. 1987
Germany	800	4,000	0.20	NA	800	NA	vanDijk and Roncken 1997
Germany	1,400 to 7,480	4,200 to 19,600	NA	6.7 to 9.3	500 to 2,700	1,330 to 12,500	Albers and Kayser 1987
Hong Kong, China	7,300	17,000	0.43	7.0 to 8.3	3,000	NA	Lo 1996
Hong Kong, China	5,000	13,000	0.38	6.8 to 9.1	11,000	NA	Lo 1996
Hong Kong, China	22,000	50,000	0.44	7.8 to 9.0	13,000	NA	Lo 1996
Hong Kong, China	4,200	15,700	0.27	7.7	2,260	NA	Lau et al. 2001
Italy	1,200	3,840	0.31	8	NA	NA	Chianese et al. 1999
Poland	331	1,180	0.28	8.0	743	NA	Bohdziewicz et al. 2001

Table 2.1 Continued...

Switzerland	250 to 350	450 to 1,500	NA	NA	300 to 600	NA	Karrer et al. 1997
Turkey	10,800 to 11,000	16,200 to 20,000	NA	7.3 to 7.8	1,120 to 2,500	7,050 to 12,100	Timur et al. 2000
	21,000 to 25,000	35,000 to 50,000	NA	5.6 to 7.0	2,020	11,500 to 13,100	
United Kingdom	3,040	5,030	0.60	5.95	76	NA	Robinson and Maris 1985
	11,900	23,800	0.50	6.21	790	NA	
	260	1,160	0.22	7.45	370	NA	
United Kingdom	7,250	11,600	0.63	7.1	340	NA	Robinson 1984
United Kingdom	3,670	5,520	0.67	5.8	130	NA	Robinson and Grantham 1988
	3,500	5,400	0.65	5.9	158	NA	
	7,000	9,750	0.72	6.3	175	NA	
United Kingdom	167	989	0.17	7.3	750	NA	Robinson 1988
	388	1,430	0.27	7.3	784	NA	
United Kingdom	1,660	4,140	0.40	NA	87	NA	Maris et al. 1985
	10,700	13,300	0.81	NA	590	NA	
United States	24,700	30,500	0.81	5.4	700	NA	Gaudy et al. 1986
United States	1,603	3,240	0.50	NA	NA	1,430	McShane et al. 1986
United Sates	30,000	52,000	0.58	6.0 to 6.5	NA	16,800	Carter et al. 1984

Notes:

NA: Not available, the same in Tables 2.2 to 2.8, and Table 2.10.

[a]Oxidation-reduction potential: 333 mV (The sign of the oxidation-reduction potential was unknown).

Table 2.2 BOD, COD, BOD/COD, pH, NH_3-N and alkalinity of old or biologically treated landfill leachates.

Location of landfill	BOD, mg/L	COD, mg/L	BOD/COD	pH	NH_3-N, mg/L as N	Alkalinity, mg/L as $CaCO_3$	Reference
Australia	60	1,100	0.06	NA	880	NA	Doyle et al. 2001
Belgium	43	895	0.05	8.2	626	NA	Geenens et al. 2001
Canada	25 to 84	207 to 440	NA	7.30 to 7.81	50 to 310	1,020 to 2,290	Ilies and Mavinic 2001
France	16.5	550	0.03	7.5	390	NA	Trebouet et al. 2001
	215	2,150	0.10	7.5	790	NA	
France	15 to 25	450 to 620	< 0.1	7.2 to 8.5	355 to 435	NA	Trebouet et al. 1999
	40 to 50	530 to 600	< 0.1	7 to 8	110 to 350	NA	
France	170	1,400	0.12	8.3	710[a]	NA	Baig and Liechti 2001
France	210	2,300	0.09	8.4	564	4,160	Bigot et 1994
France[b]	70	1,350	0.01	8.24	500	NA	Millot et al. 1987
Germany	8.4	460	0.02	NA	370[c]	NA	Barratt et al. 1997
	14.4	1,070	0.01	NA	67[c]	NA	
Germany	< 10	1,000 to 1,200	< 0.01	NA	< 5	600 to 900[d]	Steensen 1997
	< 10	350 to 900	< 0.28	NA	< 5	1,500 to 2,200[d]	
	< 10	800 to 1,200	< 0.01	NA	< 5	1,300 to 2,800[d]	
Germany	3 to 5	1,150	0.00	8.4	NA	NA	Kim et al. 1997
Germany	100	1,280	0.08	7.3 to 7.7	5 to 7[e]	NA	Ince 1998
Germany	NA	1,800	NA	7.7	285	NA	Peters 1998
Hong Kong, China	100	1,660	0.06	7.1 to 8.3	2,000	NA	Lo 1996
Hong Kong, China	81	750	0.11	7.8 to 7.9	760	NA	Lo 1996
Hong Kong, China	160	1,700	0.09	7.9 to 8.1	2,300	NA	Lo 1996
Hong Kong, China	75	1,500	0.05	8.5	2,540	NA	Lau et al 2001
Japan	1 to 26	86 to 221[f]	NA	7.6 to 9.0	104 to 332	NA	Imai et al. 1998

Table 2.2 Continued …

Korea	170 to 280	1,500 to 2,100	0.11 to 0.17	7.8 to 7.9	1,290 to 1,320[e]	4,050 to 5,700	Kim et al. 2001
Korea	87	2,000	0.04	8.2	1,390	NA	Kim and Huh 1997
Korea	30	1,500	0.02	8.7	1,300	5,900	Kang Hwang 2000
Korea	2,920	26,000	0.11	7.8	1,850	12,300	Qureshi et al. 2002
Korea	50 to 70	1,200 to 1,500	<0.05	6.8 to 7.5	NA	NA	Yoo et al. 2001
Slovakia	80	5,300	0.15	7.8	470	NA	Derco et al. 2002
Taiwan, China	50 to 270	1,050 to 2,020	NA	7.03 to 8.64	200 to 3,400	NA	Gau and Chang 1996
Taiwan, China	194	1940	0.10	8.1	151	NA	Lin and Chang 2000
Thailand	230	4,000	0.06	8.5	NA	NA	Sandya et al. 1995

Notes:

[a]Kjeldahl nitrogen;

[b]Oxidation-reduction potential: +260 mV;

[c]Total nitrogen;

[d]As HCO_3^-, mg/L;

[e]Total Kjieldahl nitrogen;

[f]COD_{Mn}.

2.3 Mechanisms of advanced oxidation processes

In general, ozone oxidation can go through either molecular ozone reactions or •OH radical reactions depending on the composition and pH of the wastewater. The •OH radical reaction is the major pathway of O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+}, and H_2O_2/Fe^{2+}/UV oxidation processes.

2.3.1 Ozone (O_3)

In aqueous solutions, ozone may act on various compounds in the following two reaction pathways (Hoigné and Bader 1978): direct reaction with the molecular ozone, and indirect reaction with the radical species that are formed when ozone decomposes in water.

2.3.1.1 Molecular ozone reactions

Molecular ozone reactions can be performed via cyclo addition, electrophilic reaction, or nucleophilic reaction (Bailey and Trahanovsky 1978). These reactions have been described in details by Langlais et al. (1991):

1) In cyclo addition, ozone molecules may react on unsaturated bonds (C=C, C=C–O–R, –C=C–X) resulting in carbonyl compounds (aldehyde or ketone) and hydrogen peroxide, H_2O_2.

2) Electrophilic reaction is restricted to certain aromatic compounds with a strong electron density. For the aromatics substituted with electron donor groups (such as –OH, $–NH_2$), the initial attack of ozone molecules occurs at ortho- and para- positions. The final products of this type of reactions are quinoid (for example, pyridoxine), and aliphatic products with carbonyl and carboxyl function groups. On the

other hand, for the aromatics substituted with electron withdrawing groups (–COOH, $–NO_2$), the initial attack of the ozone molecules takes place on the least deactivated meta- position.

3) Nucleophilic reaction is found locally on molecular sites showing an electronic deficit, and more frequently, on carbons carrying electron-withdrawing groups.

Therefore, the molecular ozone reactions are extremely selective and limited to aromatic compounds (benzene, toluene) and unsaturated aliphatic compounds (ethylene, vinyl chloride, dichloroethylene, trichloroethylene, tetrachloroethylene), as well as to specific functional groups (Langlais et al. 1991).

2.3.1.2 •OH radical reactions

The stability of dissolved ozone is readily affected by pH, UV radiation, ozone concentration, and the concentration of radical scavengers (Tomiyasu et al. 1985). Two mechanisms that describe ozone decomposition have been put forward: the Hoigné, Staehelin and Bader mechanism and the Gordon, Tomiyasu and Fukutomi mechanism (Langlais et al. 1991).

According to the Hoigné, Staehelin and Bader mechanism, ozone decomposition occurs in a chain reaction process that can be represented by the following fundamental reactions (Weiss 1935; Staehelin et al. 1984):

[1] $O_3 + OH^- \rightarrow \bullet HO_2 + \bullet O_2^-$

[2] $\bullet HO_2 \leftrightarrow \bullet O_2^- + H^+$

[3] $O_3 + \bullet O_2^- \rightarrow \bullet O_3^- + O_2$

[4] $\bullet O_3^- + H^+ \leftrightarrow \bullet HO_3$

[5]$\bullet HO_3 \rightarrow \bullet OH + O_2$

[6]$\bullet OH + O_3 \rightarrow \bullet HO_4$

[7]$\bullet HO_4 \rightarrow \bullet HO_2 + O_2$

[8]$\bullet HO_4 + \bullet HO_4 \rightarrow H_2O_2 + 2\ O_3$

[9]$\bullet HO_4 + \bullet HO_3 \rightarrow H_2O_2 + O_3 + O_2$

The free-radical initiating step constitutes the rate-limiting step in this group of reactions. The regeneration of $\bullet O_2^-$ or its protonic form $\bullet HO_2$ from the •OH radical will consume one mole of ozone. As a result, all the species capable of consuming •OH radicals without regenerating $\bullet O_2^-$ will impose a stabilizing effect on the ozone molecules in water.

According to the Gordon, Tomiyasu and Fukutomi mechanism, another set of reactions has been proposed to represent the decomposition of aqueous ozone (Tomiyasu et al 1985; Grasso 1987). Compared to that of the Hoigné, Staehelin and Bader mechanism, the two intermediates $\bullet HO_3$ and $\bullet HO_4$ were not proposed in this mechanism. This mechanism is represented by the following set of reactions:

[10]$O_3 + OH^- \rightarrow \bullet HO_2^- + O_2$

[11]$\bullet HO_2^- + O_3 \rightarrow \bullet O_3^- + \bullet HO_2$

[12]$\bullet HO_2 + OH^- \leftrightarrow \bullet O_2^- + H_2O$

[13]$\bullet O_2^- + O_3 \rightarrow \bullet O_3^- + O_2$

[14]$\bullet O_3^- + H_2O \rightarrow \bullet OH + O_2 + OH^-$

[15]$\bullet O_3^- + \bullet OH \rightarrow \bullet O_2^- + \bullet HO_2$

[16]$\bullet O_3^- + \bullet OH \rightarrow O_3 + OH^-$

[17]$\bullet OH + O_3 \rightarrow \bullet HO_2 + O_2$

[18]$\bullet OH + CO_3^{2-} \rightarrow OH^- + \bullet CO_3^-$

[19]$\bullet CO_3^- + O_3 \rightarrow CO_2 + \bullet O_2^- + O_2$

The scavengers of the free radicals are compounds capable of consuming •OH radicals without regenerating the superoxide anion $\bullet O_2^-$ (Langlais et al. 1991). The common scavengers of free radicals include alkyl groups, tertiary alcohols, humic substances, carbonate, and bicarbonate (Hoigné et al. 1985). Therefore, a lower pH is favourable for the processes based on •OH radical oxidations. The scavenging effect of carbonate and bicarbonate can be described using the following reactions:

[20]$\bullet OH + CO_3^{2-} \rightarrow OH^- + \bullet CO_3^-$ (Buxton et al. 1988)

[21]$\bullet OH + HCO_3^- \rightarrow H_2O + \bullet CO_3^-$ (Buxton et al. 1988)

2.3.2 Ozone with hydrogen peroxide (O_3/H_2O_2)

Hydroxyl (•OH) radicals can be formed with O_3 and H_2O_2 through a complex set of reactions (Langlais et al. 1991). Those reactions result in the formation of two •OH radicals from one H_2O_2 and two O_3 molecules as an overall reaction (Schulte et al. 1995).

[22]$H_2O_2 + H_2O \leftrightarrow \bullet HO_2^- + H_3O^+$

[23]$O_3 + \bullet HO_2^- \rightarrow \bullet OH + \bullet O_2^- + O_2$

[24]$\bullet O_2^- + H^+ \leftrightarrow \bullet HO_2$

[25]$O_3 + \bullet O_2^- \rightarrow \bullet O_3^- + O_2$

[26]$\bullet O_3^- + H^+ \leftrightarrow \bullet HO_3$

[27]$\bullet HO_3 \rightarrow \bullet OH + O_2$

[28]$H_2O_2 + 2O_3 \rightarrow 2 \bullet OH + 3\ O_2$ (overall reaction)

2.3.3 Ozone with ultraviolet radiation (O_3/UV)

Hydroxyl (•OH) radicals can also be formed with O_3 combined with UV radiation. O_3 can absorb UV radiation at the wavelength of 200 to 300 nm. The maximum UV absorbance by O_3 is at 253.7 nm (Langlais et al. 1991). The UV radiation of ozone causes the release of a molecule of oxygen and an atom of oxygen as $O(^1D)$. The latter will react with water and form two •OH radicals (McGrath and Norrish 1960):

[29] $O_3 + h\upsilon \rightarrow O_2 + O(^1D)$

[30] $O(^1D) + H_2O \rightarrow 2\ \bullet OH$

2.3.4 Hydrogen peroxide with ultraviolet radiation (H_2O_2/UV)

In the process of H_2O_2/UV oxidation, •OH radicals are formed by hemolytic splitting of the oxygen-oxygen bonds of H_2O_2 by UV radiation at a wavelength (λ) of 200 to 300 nm (Bolton 1999). For the photolysis of H_2O_2 with UV at a wavelength of 297 to 365 nm, •OH radicals account for all the primary decomposition of H_2O_2 (Jacob et al. 1977):

[31] $H_2O_2 + h\upsilon \rightarrow 2\ \bullet OH$

For this process, higher level of H_2O_2 and UV lamp with strong output in the range of 200 to 300 nm are required because of the small molar UV absorption coefficient of H_2O_2 within the wavelength range of 200 to 300 nm.

2.3.5 The Fenton process (H_2O_2/Fe^{2+})

The activating reaction of H_2O_2 with Fe^{2+} is known as the Fenton reaction. In this reaction, H_2O_2 decomposition is enhanced by Fe^{2+}, and •OH radicals are formed (Harber and Weiss 1934):

[32] $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \bullet OH$

[33] $H_2O_2 + \bullet OH \rightarrow H_2O + \bullet HO_2$

[34] $\bullet HO_2 + H_2O_2 \rightarrow O_2 + H_2O + \bullet OH$

[35] $\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-$

Generally, the Fenton process is composed of four stages: pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation (Bigda 1995). In contrast to other activated H_2O_2 processes, iron hydroxide is precipitated and has to be discarded. Therefore, the cost for chemical sludge disposal has to be taken into consideration during the economical assessment of the Fenton process.

2.3.6 The photo-Fenton process or photo-assisted Fenton process ($H_2O_2/Fe^{2+}/UV$)

The photo-Fenton process or photo-assisted Fenton process (a combination of H_2O_2/UV with Fe^{2+} or Fe^{3+} oxalate) can produce an increased concentration of •OH radicals from the photolysis of aqueous Fe^{3+} species. Photolysis of Fe^{3+} complex (Fe^{3+} hydroxyl complex ($Fe(OH)^{2+}$) and Fe^{3+} oxalate complex ($Fe(C_2O_4)_3^{3-}$)) takes place very rapidly under irradiation with near UV and even visible light.

[36] $Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + \bullet OH$

The quantum yield of $Fe(OH)^{2+}$ in reaction [36] was 0.14 at 313 nm and 0.017 at 360 nm under the condition of pH = 4.0, and 293 K (Faust and Hoigné 1990).

Fe^{3+} oxalate complexes ($Fe(C_2O_4)_3^{3-}$) are also photo-reactive and exhibit an increased quantum yield of 1.2 at 313 nm when 1 kW high-pressure mercury UV lamp was used and exposure time was 1.5 to 6.0 min (Hatchard and Parker 1956).

[37] $Fe(C_2O_4)_3^{3-} + h\upsilon \rightarrow Fe^{2+} + 2\ C_2O_4^{2-} + \bullet C_2O_4^-$

[38] $\bullet C_2O_4^- + Fe(C_2O_4)_3^{3-} \rightarrow Fe^{2+} + 3\ C_2O_4^{2-} + 2\ CO_2$

[39] $\bullet C_2O_4^- + O_2 \rightarrow \bullet O_2^- + 2\ CO_2$

The Fe^{2+} ions formed by the photo-reduction of Fe^{3+} complexes in reactions [36] to [38] will participate in the Fenton reactions as shown in reactions [32] to [35].

2.4 Advanced oxidation of landfill leachates

COD and BOD before oxidation, COD removal efficiency, the ratio of BOD/COD after oxidation, and the oxidant dose of O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+}, and $H_2O_2/Fe^{2+}/UV$ treatments of landfill leachate are summarized in Tables 2.3 to 2.8. The colour removal efficiencies when these processes were applied to treat landfill leachate are shown in Table 2.9.

2.4.1 COD removal efficiency

Based on the published data shown in Tables 2.3 to 2.8, the COD removal efficiencies, during the O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+}, and $H_2O_2/Fe^{2+}/UV$ treatments, are summarized in Table 2.10. Such a wide COD removal efficiency range may have been caused by the following factors. Firstly, different oxidant doses; secondly, specific leachate characteristics; thirdly, leachate pH when the oxidation took place; and finally, the concentrations of carbonate and bicarbonate, especially for the oxidation processes based on the •OH radical reaction. Usually, laboratory-scale comparative tests are performed to evaluate the efficiency of each advanced oxidation process on a specific landfill leachate (Geenens et al. 2001). Furthermore, a trade-off between the organic pollutant removal efficiency, the complexity of the process-train and the operational cost should be considered.

Table 2.3 Application of ozonation in landfill leachate treatment.

COD, mg/L	BOD, mg/L	pH	R_{COD}[a], %	BOD/COD[b]	O_3/COD[c], g/g	Reference
4,000	230	8.5	25	NA	0.53	Sandya et al. 1995
740	240	NA	NA	NA	NA	Hausler et al. 1995
640	205[d]	NA	NA	0.40	1.28 to 1.92	Fettig et al. 1996
500	30	7	NA	140 mg/L[e]	0.11	Karrer et al. 1997
460	NA	NA	71	NA	1.8	Barratt et al. 1997
1,050	NA	8.5	67	NA	1.7	Barratt et al. 1997
151[f]	5	8.1	33	0.35	NA	Imai et al. 1998
300 to 1,200	<10	7.0 to 8.0	80	NA	3.0	Steensen 1997
895	43	8.2	30	0.11	1.11	Geenens et al. 2001
518	NA	8.3	66	NA	1.7	Baig and Liechti 2001
3,500	25	8.2	67	0.21	0.7[g]	Derco et al. 2002
2,300	210	8.0	62	NA	1.5	Bigot et al. 1994
2,300	210	3.0	50	NA	0.5	Bigot et al. 1994
2,300	210	8.0	50	NA	1.0	Bigot et al. 1994
14,600	2,920	7.8	56	0.32	3.1[h]	Qureshi et al. 2002

Notes:

[a]COD removal efficiency, the same in Tables 2.4 to 2.8;

[b]BOD/COD after oxidation treatment, the same in Tables 2.4 to 2.7;

[c]Ratio of O_3/COD is the mass of ozone in inlet gas to the mass of the initial COD, unless indicated;

[d]Dissolved organic carbon (DOC);

[e]BOD_5 after ozonation, determined by measuring the partial pressure drop of oxygen in the headspace of reaction vessel;

[f]COD_{Mn} (chemical oxygen demand determined with potassium permanganate);

[g]Mass of O_3 consumed to the mass of initial COD;

[h]Ratio of TOC removed to O_3 (It is unknown whether the used-ozone mass or applied-ozone mass).

Table 2.4 Application of O_3/H_2O_2 in landfill leachate treatment.

COD, mg/L	BOD, mg/L	pH	R_{COD}, %	H_2O_2/O_3, g/g	BOD/COD	O_3/COD, g/g	Reference
2,000	NA	NA	95	0.4	NA	3.5[a]	Wable et al. 1993
600	NA	NA	92	0.4	NA	3.3[a]	Wable et al. 1993
NA	NA	8	97	1.0[b]	NA	2.5g/L[c]	Schulte et al. 1995
NA	NA	8	70	0.5[b]	NA	NA	Schulte et al. 1995
895	43	8.2	28	NA	0.14	0.76	Geenens et al. 1999
2,000	160	8.4	92[d]	0.3	0.13	1.5	Bigot et al. 1994
1,360	<5	8.4	93[d]	0.3	0.32	1.5	Bigot et al. 1994

Notes:

[a]Transferred ozone mass to mass of initial COD;

[b]It is unknown whether this ratio is mass ratio or molar ratio;

[c]Ozone dose;

[d]Heterogeneous catalytic ozonation with H_2O_2.

Table 2.5 Application of O_3/UV in landfill leachate treatment.

COD, mg/L	BOD, mg/L	pH[a]	R_{COD}, %	BOD/COD	UV, W	O_3/COD, g/g	Reference
1,280	100	2.0	54	NA	100	NA	Ince 1998
1,280	100	2.0	47	NA	500	NA	Ince 1998
26,000	2,920	7.8	63[b]	0.32	1,500	3.5[c]	Qureshi et al. 2002
26,000	2,920	7.8	61[b]	0.35	1,500	4.7[c]	Qureshi et al. 2002
2,300	210	8.0	50	NA	15	1.0	Bigot et al. 1994

Notes:

[a]Treatment pH;

[b]Removal efficiency of TOC, the TOC concentration of raw leachate was 14,616 mg/L;

[c]Ratio of TOC removed to O_3 (It is unknown whether the used-ozone mass or applied ozone mass).

Table 2.6 Application of H_2O_2/UV in landfill leachate treatment.

COD, mg/L	BOD, mg/L	pH[a]	R_{COD}, %	BOD/COD	UV, W	H_2O_2, g/L	Reference
760	NA	NA	22[b]	NA	150	3.4	Schulte et al. 1995
760	NA	3	99[c]	NA	150	3.4	Schulte et al. 1995
1,280	100	2	57	NA	100	NA	Ince 1998
1,280	100	2	59	NA	500	NA	Ince 1998
1,000 to 1,200	<10	3.0 to 4.0	90	NA	15	0.5	Steensen 1997
1,000 to 1,200	<10	3.0 to 4.0	85	NA	150	0.5	Steensen 1997
14,600[d]	2,920	3.0	79[e]	0.37	1,500	5.19	Qureshi et al. 2002
14,600[d]	2,920	3.0	91[e]	0.40	1,500	13.0	Qureshi et al. 2002
14,600[d]	2,920	3.0	96[e]	0.45	1,500	26.0	Qureshi et al. 2002

Notes:

[a]Optimum pH;

[b]With carbonate;

[c]Without carbonate;

[d]TOC concentration of raw leachate, the COD of raw leachate was 26,000 mg/L;

[e]Removal efficiency of TOC.

Table 2.7 Application of H_2O_2/Fe^{2+} in landfill leachate treatment.

COD, mg/L	BOD, mg/L	pH[a]	R_{COD}, %	BOD/COD	Fe^{2+}, mg/L	H_2O_2, g/L	Reference
1,050 to 2,020	50 to 270	4.0	60	NA	600 to 800	0.2	Gau and Chang 1996
1,150	3 to 5	3	70	NA	56	2.44	Kim et al. 1997
2,000	87	3.5	69	0.58	120	1.5	Kim and Huh 1997
282 to 417[b]	NA	3	49 to 76[c]	NA	1,250	1.0	Yoon et al. 1998
NA	NA	3	50	NA	NA	1.6	Schulte et al. 1995
NA	NA	3	55	NA	NA	2.2	Schulte et al. 1995
1,800	225	3	52	0.22	2,000	1.5	Kim et al. 2001
1,800	225	4.5	45	0.27	1,500[d]	1.2	Kim et al. 2001
1,500	75	6	70	NA	300	0.2	Lau et al. 2001
1,500	30	3.5	75	NA	645	1.65	Kang and Hwang 2000

Notes:

[a]Optimum pH;

[b]TOC concentration;

[c]TOC removal efficiency;

[d]Fe^{3+} dose.

Table 2.8 Application of H_2O_2/Fe^{2+}/UV in landfill leachate treatment.

No.	COD mg/L	BOD mg/L	pH[a]	R_{COD} %	UV W	Fe^{2+} mg/L	H_2O_2 g/L	Reference
1	1,150	3 to 5	3.0	70	500 or 1000	56	1.15	Kim et al 1997
2	1,150	NA	3.2	70	UVA	72	1.15	Kim and Vogelpohl 1998
3	440	NA	2.7	78	UVA	30[b]	0.44	Kim and Vogelpohl 1998

Notes:

[a]Optimum pH;

[b]Fe^{3+} dose.

Table 2.9 Colour removal efficiency.

No.	Process	Colour	pH	R_{colour}[a], %	Oxidant dosage	Reference
1	O_3	15,000[b]	8.5	90	0.53 g O_3/g COD	Sandya et al. 1995
2	O_3	1.062[c]	3	100	0.75 g O_3/g COD	Bigot et al. 1994
3	O_3	1.062[c]	8	90	0.75 g O_3/g COD	Bigot et al. 1994
4	O_3/UV	1.062[c]	8	78	0.75 g O_3/g COD	Bigot et al. 1994
5	H_2O_2/Fe^{2+}	2.8[d]	3.5	91	H_2O_2: 1,500 mg/L Molar ratio of Fe^{2+}/H_2O_2: 0.08	Kim and Huh 1997
6	O_3[e]	6,140[f]	7.8	52	0.10 g O_3/g COD	Qureshi et al. 2002
7	O_3/UV[e]	6,140[f]	7.8	87	0.07 g O_3/g COD	Qureshi et al. 2002
8	O_3/UV[e]	6,140[f]	7.8	88	0.10 g O_3/g COD	Qureshi et al. 2002
9	H_2O_2/UV[e]	5,080[g]	3.0	96	0.2 g H_2O_2/g COD	Qureshi et al. 2002
10	H_2O_2/UV[e]	5,080[g]	3.0	98	0.5 g H_2O_2/g COD	Qureshi et al. 2002
11	H_2O_2/UV[e]	5,080[g]	3.0	99	1.0 g H_2O_2/g COD	Qureshi et al. 2002

Notes:

[a]Colour removal efficiency;

[b]Colour unit, °Hazen, equals to TCU;

[c]Absorbance at 460 nm;

[d]Absorbance at 380nm;

[e]UV lamp input 1,500 W;

[f]Pt-Co unit, pH = 7.8;

[g]Pt-Co unit, pH = 3.0.

Table 2.10 Summary of COD removal efficiencies and ratios of BOD_5/COD after oxidation of O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+} and H_2O_2/Fe^{2+}/UV

Process	COD removal efficiency, %	Ratio of BOD/COD after oxidation	Data source
O_3	25 to 80	0.11 to 0.35	Table 2.3
O_3/H_2O_2	28 to 97	0.13 to 0.32	Table 2.4
O_3/UV	47 to 63	0.32 to 0.35	Table 2.5
H_2O_2/UV	22 to 99	0.37 to 0.45	Table 2.6
H_2O_2/Fe^{2+}	45 to 75	0.22 to 0.58	Table 2.7
H_2O_2/Fe^{2+}/UV	70 to 78	NA	Table 2.8

When ozonation process is applied for landfill leachate treatment (see Table 2.3), COD removal efficiency varies from 25% to 80%, and is around 50% to 71% in most cases. Therefore, ozonation alone can hardly achieve the discharge requirements unless a high ozone dose is applied.

For the O_3/H_2O_2 process (see Table 2.4), COD removal efficiency can be as high as 90% and usually achieved at the mass ratio of H_2O_2 to O_3 at 0.3 to 0.4 g H_2O_2/g O_3 (Bigot et al. 1994; Wable et al. 1993). According to Equation [28], the theoretical stoichiometric mass ratio of H_2O_2 to O_3 equals 0.354 to produce •OH radicals. COD removal efficiency of only 28% (Geenens et al. 1999) might have been caused by either low O_3/COD ratio or improper H_2O_2/O_3 ratio. Since it was not indicated in Schulte et al.

(1995) whether the H_2O_2/O_3 ratio was mass ratio or molar ratio, the low COD removal efficiency of 70% might have been due to an improper H_2O_2/O_3 ratio.

Based on the experimental results of Ince (1998), COD removal efficiency of H_2O_2/UV process ranged from 57% to 59% (see Table 2.6). The COD removal efficiency reported by Ince (1998) is lower than those results of other researchers. This might have been due to the H_2O_2 residue being removed by sodium thiosulphate ($Na_2S_2O_3$) in Ince's experiments, whereas, it was removed by Bovine liver catalase in other researchers' experiments. During the course of COD measurement, the oxidation-reduction reactions take place where substances, whose oxidation-reduction potentials are lower than that of potassium dichromate ($K_2Cr_2O_7$), are oxidized, and Cr^{6+} is reduced to Cr^{3+}. Therefore, similar to H_2O_2 (Kang et al. 1999), when $Na_2S_2O_3$ is used to remove the residue of H_2O_2, the residue of $Na_2S_2O_3$ will also react with $K_2Cr_2O_7$ and gives rise to the increase in measured COD, thus leading to lower COD removal efficiencies than those obtained during other case studies of H_2O_2/UV treatment.

If the adverse influence of bicarbonate and carbonate on the oxidation of leachate with H_2O_2/UV can be excluded by lowering the pH of the leachate to the range of 3.0 to 4.0 (Schulte et al. 1995), and ruling out Ince's results, H_2O_2/UV treatment should always give COD removal efficiency higher than 80%, according to the data from the published literature (see Table 2.6).

In addition to carbonate and bicarbonate, other important factors, which severely affect the COD removal efficiency of the H_2O_2/UV process, are the background absorbance and particle concentration of leachate. Therefore, good COD removal efficiencies during landfill leachate treatment can only be obtained at a high H_2O_2 dose

and long exposure time of UV radiation with medium- or high-pressure lamps at wavelength of 200 to 300 nm (Bolton 1999).

2.4.2 Ratio of BOD/COD after oxidation

Occasionally, instead of focusing only on COD removal, another objective of advanced oxidation processes, when applied for treating landfill leachate, is to enhance its biodegradability (i.e., the ratio of BOD/COD) so that the biodegradable organic pollutants can be removed in a subsequent biological process, which is much cheaper than advanced oxidation processes. Based on the data shown in Tables 2.3 to 2.8, the ratio of BOD/COD after treatment with O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, and H_2O_2/Fe^{2+} is summarized in Table 2.10. If the biodegradability of leachate is judged by the ratio of BOD/COD after oxidation, it seems that ozonation does not have any advantage over O_3/H_2O_2, O_3/UV, H_2O_2/UV, and H_2O_2/Fe^{2+} in improving the leachate biodegradability. On the contrary, according to the published data, H_2O_2/UV treatment stands out, in comparison to other advanced oxidation processes, in terms of improving the leachate biodegradability.

For the products of ozonation, a widely accepted viewpoint is that the ozone will break down the large refractory organic molecules and form small biodegradable organic molecules (Langlais et al. 1989; Langlais et al. 1991; Beltran-Heredia et al. 2000; Baig and Liechti 2001; Geenens et al. 2001). The small biodegradable organic molecules can then be utilized by microorganisms during their metabolic processes. Therefore, a partial oxidation of the refractory organics to easily biodegradable by-products is preferred to improve the biodegradability of the landfill leachate. However, it should not be forgotten that the classical ozone chemistry was based on the experimental results of the ozonation

of slightly polluted natural water or single model compound. For a very complex matrix such as landfill leachate, sufficient experimental evidence is needed to verify whether ozone transforms large molecules into small molecules or it oxidizes large molecules directly to the end products, such as carbon dioxide and water.

It is believed that the O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+} and H_2O_2/Fe^{2+}/UV oxidation processes mainly take the •OH reaction pathway because of the synergistic effects between O_3 and H_2O_2, or O_3 and UV, or between H_2O_2 and UV and/or Fe^{2+}. As a result, •OH radicals can lead to complete breakdown of organic pollutants. However, the reported BOD/COD experimental data obtained from the advanced oxidation processes (O_3/H_2O_2, O_3/UV, H_2O_2/UV, and H_2O_2/Fe^{2+} oxidation processes) for landfill leachate treatment do not seem to support such a conclusion (see Tables 2.3 to 2.7). The free radical oxidation mechanisms presented in this research are mostly based on the classical reactions in potable waters. In a complex matrix such as landfill leachate, more free radicals may be formed, and more scavengers may be present as well. Therefore, further research is necessary to analyze the leachate oxidation products of O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+} and H_2O_2/Fe^{2+}/UV oxidation processes.

In addition to BOD and the ratio of BOD/COD, gel filtration chromatography is a potentially valuable technique to reveal the change in molecular size distribution before and after oxidation since it can reflect the disappearance of large molecules and the formation of small molecules. To get a well-separated chromatogram, a caution must be taken in the selection of gel filtration column, the determination of type and concentration of salt in the eluant (Ceccanti et al. 1989) and the eluant flow rate. The disadvantage of gel filtration chromatography is that it is difficult to find the molecular size standards,

which have exactly the same characteristics as the analytes. Therefore, it is hard to directly make credible molecular size measurement (Gaffney et al. 1996). Fortunately, measurement of true molecular size is of less importance than relative distribution of different molecules (Ceccanti et al. 1989).

Chian (1977) and Lecoupannec (1999) used gel filtration chromatography to measure the molecular size distribution of compounds present in landfill leachate. Imai et al. (1998) and Gau and Chang (1996) analyzed the change in molecular size distribution of landfill leachate before and after oxidation with O_3 and H_2O_2/Fe^{2+}, respectively. Nevertheless, the data on the molecular size distribution of landfill leachate before and after oxidation with O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+} and H_2O_2/Fe^{2+}/UV still remain very limited. Moreover, the gel filtration column, the type and the concentration of salt in the eluant and the eluant flow rates that have been used are not exactly the same for various research studies. Therefore, the data can hardly be compared. Hence, it would be valuable if molecular size distributions before and after oxidation with O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+} and H_2O_2/Fe^{2+}/UV were measured under the same gel filtration chromatograph operating conditions.

2.4.3 Colour removal efficiency

The young landfill leachates tend to have a black colour, while the old or biologically treated landfill leachates have a dark brown or yellow colour. To meet the discharge standards, colour reduction is also one of the objectives of the landfill leachate oxidation treatment. Colour removal efficiency achieved during O_3, O_3/UV, H_2O_2/UV, and H_2O_2/Fe^{2+} oxidation treatments ranged from 52% to 100% (see Table 2.9).

The lower colour removal efficiency of 52%, reported by Qureshi et al. (2002),

might have been due to the fact that some of colour-causing compounds in this leachate were insensitive to the attack of molecular ozone. When O_3/UV was applied on this leachate, the colour removal efficiency increased from 52% at an ozone dose of 0.10 g O_3/g COD for O_3 only, to 87% at ozone dose of 0.07 g O_3/g COD for O_3/UV oxidation process. Moreover, for the O_3/UV process, when ozone dose increased from 0.07 g O_3/g COD to 0.10 g O_3/g COD, the colour removal efficiency increased only by 1%.

The low colour removal efficiency of 78% obtained by Bigot et al. (1994), during an O_3/UV oxidation process conducted at a pH of 8, might have been caused by the high concentration of carbonates (4,000 mg $CaCO_3$/L) which is a scavenger of the •OH radicals.

Therefore, the colour removal efficiency seems to depend on the characteristics of the colour-causing compounds as well as the treatment process. If the chromophores of colour-causing compounds are double bonds or benzene structures, high colour reduction can be achieved by O_3 only. Otherwise, the advanced oxidation processes based on •OH radical reactions should be selected and run at a proper pH to achieve high colour reduction.

2.4.4 Limitations of advanced oxidation processes

Ozone gas is usually produced from extra dry oxygen gas or air by high voltage discharge. Therefore, the energy demand is quite high. Moreover, ozone mass transfer from gas into liquid is involved in all of the ozone-related processes such as O_3, O_3/H_2O_2, and O_3/UV oxidation processes. Although much effort has been devoted to enhance the ozone mass transfer efficiency (Barratt et al. 1997; Gamal El-Din and Smith 2001), the ozone utilization rate by the oxidation is still relatively low as some of the ozone is lost in

the off-gas exiting from the ozone reactor, especially at high applied-ozone doses. As a result, a catalytic ozone destruction unit is needed. For a complex matrix with high organic content such as landfill leachate, ozonation can hardly meet the discharge standards unless a high ozone dose is applied. Therefore, ozone only as pretreatment and followed by a biological treatment system might be a feasible polishing process for old or biologically treated landfill leachate containing a large fraction of refractory organic compounds.

UV radiation is often used as an initiator of the •OH radical production. If UV related processes (such as O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+}/UV) are applied in full-scale leachate treatment systems, the following problems might be encountered: (1) Sparingly soluble oxalates will form a scale layer on the UV lamps due to the high carbonate and bicarbonate concentrations, thus reducing the effectiveness of UV lamps (Steensen 1997); (2) The suspended solids (Loge et al. 1999) or contaminants with high UV absorbance (Bigot et al. 1994) in landfill leachate can block or absorb UV transmittance in leachate and reduce the effectiveness of UV lamps; (3) For the full-scale application of UV technology for leachate treatment, medium- or high-pressure UV lamps with wavelength of 200 to 300 nm have to be used to get an even distribution of UV radiation that will cause both high energy consumption and a small effective diameter of the ozonation reactor (Geenens et al. 1999); (4) The foam caused by ozone bubbles can also block UV penetration inside the leachate matrix, and results in low efficiency of O_3/UV treatment (Bigot et al. 1994); and (5) During the H_2O_2/UV oxidation process, the role of UV is to activate H_2O_2 and produce •OH radicals; meanwhile, if the landfill leachate has high background absorbance or a high particle concentration, this process will not work well

due to the low UV absorbance of H_2O_2.

To overcome the shortcomings of O_3/UV and H_2O_2/UV treatments, the H_2O_2/Fe^{2+} and H_2O_2/Fe^{2+}/UV processes have been developed. In these processes, the UV, which is an expensive •OH radical initiator, is completely or partially replaced by Fe^{2+} or oxalate of Fe^{3+}, which are much cheaper than UV. However, the efficiencies of H_2O_2/Fe^{2+} and H_2O_2/Fe^{2+}/UV are not as good as that of H_2O_2/UV even under the same pH condition. In addition, chemical sludge, which results from the coagulation of suspended solids in the leachate, and iron hydroxide precipitates, formed when pH is adjusted back to an alkaline condition, need to be removed and disposed of.

The H_2O_2-related processes are not suitable for practical applications due to the slow reaction rates of H_2O_2 with organics and the slow self-decomposition rate of H_2O_2, as well as its influence on the subsequent biological treatment systems or the ecosystems of the receiving watercourses.

Although the advanced oxidation processes have the limitations mentioned above, they are still one category of effective means to deal with the refractory organic compounds in old or biologically treated landfill leachate.

2.5 Influence of ammonia nitrogen on advanced oxidation of landfill leachates

NH_3-N in landfill leachate results from the biodegradation of nitrogen-containing organic compounds such as proteins (Lo 1996). As shown in Table 2.2, the NH_3-N concentration in old or biologically treated landfill leachate varies from less than 5 to 3,400 mg/L. To date, little attention has been paid to the influence of ammonia in landfill

leachate on the oxidant demand and the overall oxidation process. Contrary conclusions were drawn from different landfill leachate oxidation case studies. Bigot et al. (1994) reported that ammonia was not affected by O_3 or O_3/H_2O_2 oxidation. Meanwhile, Karrer et al. (1997) nitrified the ammonia with fluidized sand biofilm reactor to avoid the reaction of O_3 with ammonia. Furthermore, Geenens et al. (2001) found that the high ammonia in leachate inhibited nitrification when the leachate was subjected to biological treatment. High ammonia concentrations can be toxic to nitrifiers (Cameron and Koch 1980), and ozonation can reduce the toxicity of leachate.

2.6 Influences of pH and alkalinity on advanced oxidation of landfill leachates

Most experiments involving landfill leachate ozonation were performed within a pH range of 7.0 to 8.5 (see Table 2.3). However, a COD removal efficiency of 50% was attained at 0.5 g O_3/g COD when pH of the leachate was reduced to 3 and at 1.0 g O_3/g COD when pH of the leachate was 8.0 (Bigot et al. 1994). This fact seems to show that low pH can reduce the ozone demand. However, when the pH is lowered, the ratio of used-ozone dose to applied-ozone dose will decrease, thus causing the ozone utilization rate to decrease. Moreover, landfill leachate has high alkalinity, and a lot of acid is required to decrease the pH. Therefore, a cost/benefit analysis is required before ozonation at low pH is chosen as the method of treatment.

For the O_3/H_2O_2 process, the reaction pH is in the range of 8 to 8.4 (see Table 2.4). Although the reaction pH for O_3/UV was within the range of 7.8 to 8.0 (see Table 2.5), the COD removal efficiency was quite low (around 50%). This may have been

caused by a high pH, low radiation intensity, high background absorbance (Bigot et al. 1994), or high particle concentration of the leachate (Loge et al. 1999). Furthermore, the foam caused by ozone bubbles could have also blocked the UV transmittance (Bigot et al. 1994) in leachates.

The experimental data show that the optimal pH range for H_2O_2/UV, H_2O_2/Fe^{2+}, and H_2O_2/Fe^{2+}/UV, respectively, is in the range of 2.0 to 4.0 (see Table 2.6), 3.0 to 6.0 (see Table 2.7), and 2.7 to 3.2 (see Table 2.8), respectively. This may also imply that the •OH radical reaction was the major reaction pathway of these processes.

The pH ranges from 6.8 to 9.0 for old or biologically treated raw landfill leachate and from 5.0 to 9.3 for young landfill leachate. Therefore, the major fraction of alkalinity in the landfill leachate is bicarbonate alone or bicarbonate and carbonate alkalinity (Sawyer et al. 1994). As shown in Table 2.2, the alkalinity of old or biologically treated landfill leachates range from 1,020 to 12,300 mg /L of $CaCO_3$.

Carbonate and bicarbonate are the scavengers of •OH radicals and inhibitors for ozone decay. Therefore, the influence of these two species on the oxidant demand must be considered. As shown in Equations [20] and [21], molar ratio of both $\bullet OH/CO_3^{2-}$ and $\bullet OH/HCO_3^-$ is 1. Lowering pH of leachate to less than 4.5 will greatly reduce the •OH radical consumption caused by carbonate and bicarbonate, thereby enhancing the utilization efficiency of the expensive oxidants. This can also explain why the optimal pH for H_2O_2/UV, H_2O_2/Fe^{2+}, and H_2O_2/Fe^{2+}/UV is below 4.0. On the contrary, the effect of carbonate and bicarbonate alkalinity on the ozonation of landfill leachate will not be as severe as that on the •OH radical reaction. Because of the existence of carbonate and bicarbonate, molecular ozone reaction would be the major reaction pathway of leachate

ozonation, especially when leachate pH is above 7. It would be interesting to study the oxidant demand difference with and without the existence of carbonate and bicarbonate, so that comprehensive economical comparison can be made between the two operating approaches (with and without pH adjustment before oxidation).

2.7 Removal of the oxidant residues from landfill leachate samples

For O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, H_2O_2/Fe^{2+}, and H_2O_2/Fe^{2+}/UV oxidation processes, after oxidation treatment, residues of O_3 and/or H_2O_2 may be left in the samples. Such oxidant residues will hinder bacterial action in the subsequent biological treatment unit, cause measurement errors in BOD (Kim et al. 1997) and COD (Lau et al. 2001; Kim and Vogelpohl 1998; Kim et al. 1997; Wang et al. 2000), and damage the gel filtration column during the process of molecular size distribution analysis. Therefore, the residues of ozone and/or H_2O_2 must be eliminated from the samples before subsequent BOD and COD measurements and molecular size distribution analysis.

Residual ozone can be removed by aerating the ozonated leachate with nitrogen gas (Takahashi et al. 1994), helium, or air (Tzitzi et al. 1994) for about 15 minutes since these gases are more soluble than ozone, therefore, can strip residual ozone out of the leachate solution. For research purposes, nitrogen and helium should be used since such inert gases keep the other sample contents unchanged. From a viewpoint of full-scale application, air should be chosen since it is cheap, can give adequate results, and does not require the use of compressed-gas cylinders.

The residual H_2O_2 in the oxidized leachate is troublesome since its reaction rate with organics and self-decomposition rate are very slow. The most feasible and

commonly used method to remove the residual H_2O_2 is to employ an enzyme catalase obtained from Bovine liver. This is a kind of protein that acts as a catalyst for decomposing H_2O_2 into water and oxygen while the amount of the Bovine liver catalase itself does not change before and after the decomposition of H_2O_2. Meanwhile, this catalase is easily biodegradable and oxidizable using potassium dichromate when conducting BOD and COD tests, respectively. As a result, an increase in BOD and COD values will occur. This effect can be eliminated through the development of a standard curve, which relates the amount of the Bovine liver catalase to the increase in COD (Kim and Vogelpohl 1998; Kim et al. 1997) and BOD.

H_2O_2 concentration in the leachate samples can also be measured using the iodometric method while using molybdate as a catalyst to speed up the reaction between H_2O_2 and potassium iodide (Jeffery et al. 1989). H_2O_2 can be easily oxidized by potassium dichromate during COD test. As a result, H_2O_2 can cause an increase in COD values. By doing those two tests on the same leachate sample, a correlation between H_2O_2 residual concentration and the increase in COD was obtained by Kang et al. (1999).

Compared to the Bovine liver catalase method, the molybdate catalyzed iodometric method is tedious. Hence, the Bovine liver catalase method would be the simplest and most reliable method to quantify the error in BOD and COD measurements caused by any H_2O_2 residues.

Bovine liver catalase (nominal molecular weight is 250,000 Dalton) can decompose H_2O_2 into water and oxygen. However, the Bovine liver catalase itself can deteriorate the HPLC performance if it is not eliminated before the samples are injected into HPLC. A micro-centrifugal filter has a membrane with molecular weight cut-off in

between the largest molecular weight of leachate and the molecular weight of Bovine liver catalase; therefore, it can be used to remove the catalase from the samples prior to injection into HPLC.

2.8 Conclusions

Advanced oxidation is an effective means to deal with the refractory organic compounds in old or biologically treated landfill leachates.

For a complex matrix with high concentrations of organic compounds such as landfill leachate, ozonation can hardly meet the discharge standards unless a high ozone dose is applied.

O_3/H_2O_2 treatment applied at pH of 7 to 8 and H_2O_2/UV applied at pH of 2 to 4 are better than O_3, O_3/UV, H_2O_2/Fe^{2+}, and H_2O_2/Fe^{2+}/UV treatments in terms of COD removal efficiency. H_2O_2/UV is the best treatment when judged by COD removal efficiency and the ratio of BOD/COD after oxidation if both background absorbance and particle concentration of leachate are low. However, H_2O_2-related processes are not suitable for practical applications due to its slow reaction rate with organics, its slow self-decomposition rate, and its adverse influence on the subsequent biological treatment systems or the ecosystems of the receiving watercourses.

The role of UV radiation in O_3/UV oxidation process becomes obvious only if the background absorbance and the particle concentration of leachate are very low. Treatment efficiency of O_3/UV oxidation process can also be negatively affected by the foam caused by ozone bubbles. Meanwhile, this treatment efficiency can be enhanced by eliminating carbonate and bicarbonate before oxidation with O_3/UV.

Therefore, ozone only as pretreatment and followed by a biological treatment system would be a feasible polishing process for the landfill leachate containing a large fraction of refractory organic compounds.

Many aspects with regard to advanced oxidation of landfill leachates need further investigation to examine the following aspects: (1) the influence of NH_3-N and alkalinity present in landfill leachate on oxidant demands of advanced oxidations; (2) the molecular size distribution change of landfill leachate before and after oxidation, especially for H_2O_2-related processes; (3) the oxidation by-products; (4) the effect of UV on improving the biodegradability of refractory organic compounds; and (5) the influence of particles on the role of UV light during photoassisted oxidation processes.

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CHAPTER 3 OXIDATION OF AGED RAW LANDFILL LEACHATE WITH O_3 ONLY AND O_3/H_2O_2: TREATMENT EFFICIENCY AND MOLECULAR SIZE DISTRIBUTION ANALYSIS [2]

3.1 Introduction

Landfill leachate is a complex wastewater generated when the moisture content or water content of the landfilled solid waste is larger than its field capacity. Aged raw landfill leachate refers to a landfill leachate that had been aged in a storage tank for about one year. The major components of the aged raw landfill leachate are large refractory organic molecules; i.e., humic substances, which include humic acids and fulvic acids (Chian 1977; Lecoupannec 1999) with molecular weight within 1,000 to 10,000 Dalton, because the small biodegradable molecules had been stabilized during the aging process. Chemical oxidation is the commonly used process to break down these large molecules to water and carbon dioxide, or to transform the large refractory molecules into smaller, hopefully more biodegradable molecules, which can be removed in a subsequent biological system.

In the past decade, oxidation of landfill leachate with O_3 only and O_3/H_2O_2 has been well investigated. However, these investigations mainly focused on the removal efficiencies of the bulk comprehensive parameters such as chemical oxygen demand

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(COD) (Wable et al. 1993; Bigot et al. 1994; Fazzini and Young 1994; Hausler et al. 1995; Sandya et al. 1995; Schulte et al. 1995; Barratt et al. 1997; Karrer et al. 1997; Steensen 1997; Imai et al. 1998; Baig and Liechti 2001; Geenens et al. 2001; Derco et al. 2002); colour (Bigot et al. 1994; Sandya et al. 1995; Qureshi et al. 2002); total organic carbon (TOC) (Fazzini and Young 1994; Hausler et al. 1995; Baig and Liechti 2001; Qureshi et al. 2002); dissolved organic carbon (DOC) (Fettig et al. 1996; Imai et al. 1998); and/or five-day biochemical oxygen demand (BOD_5) increase efficiency (Karrer et al. 1997; Imai et al. 1998; Geenens et al. 2001; Derco et al. 2002) by oxidation with O_3 only and O_3/H_2O_2. Although correlations between the TOC (Qureshi et al. 2002); or COD (Bigot et al. 1994; Sandya et al. 1995; Steensen 1997; Baig and Liechti 2001); or colour (Bigot et al. 1994; Sandya et al. 1995; Qureshi et al. 2002) removal efficiency and ozonation time or ozone dose were found, no models that can predict the treatment efficiency have been developed.

Usually, NH_3-N and alkalinity concentrations in aged raw landfill leachate are still very high. Little attention has focused on the changes of NH_3-N and alkalinity during the oxidation processes.

To date, most of the molecular size distribution analysis focused on the molecular size of organic compounds present in landfill leachate (Chian 1977; Lecoupannec 1999). Imai et al. (1998) analyzed the molecular size distributions of landfill leachate before and after ozonation with HPLC equipped with a gel filtration column and a UV detector. The eluant was 0.3 M NaCl in 0.1 M pH = 7 phosphate buffer at flow rate of 0.8 mL/min. There is no information available about the molecular size distribution before and after oxidation with O_3/H_2O_2.

In this research, a series of experiments were designed to investigate the impact of oxidation of aged raw landfill leachate with O_3 only and O_3/H_2O_2. These experiments were conducted at different used-ozone doses, and the COD, BOD_5, colour, NH_3-N, nitrite+nitrate, and alkalinity after oxidation were monitored. Models that relate these parameters to the used-ozone dose have been developed. Meanwhile, the molecular size distributions of the aged raw landfill leachate before and after oxidation at different used-ozone doses were also obtained. These data can lead to better understanding of the oxidation process and the role of hydrogen peroxide during oxidation of landfill leachate.

3.2 Methods and materials

3.2.1 Landfill leachate

Clover Bar Landfill Site has been accepting solid wastes since 1975, and the expected closure date for this landfill site is some time after 2006. The major fraction of the solid wastes dumped in this landfill site is municipal refuse. The aged raw landfill leachate was collected from the equalization storage tank of the Clover Bar Landfill Leachate Treatment Plant. When the leachate sample was collected, this raw landfill leachate had been stabilized in the equalization storage tank for about one year due to the pipeline modification for the five-stage rotating biological contactors (RBCs). Table 3.1 depicts the quality parameters of this leachate.

Table 3.1 The quality parameters of the aged raw landfill leachate.

Parameter	Value	Standard deviation
COD, mg/L	1,090	19
BOD_5, mg/L	39	7
Ratio of BOD_5/COD	0.04	/
Colour, TCU	1,130	7
NH_3-N, mg/L as N	455	2.0
Alkalinity, mg/L as $CaCO_3$	4,030	27
pH	8.30	0.01
Conductivity, mS/cm	15.1	0.1

3.2.2 Procedure for leachate oxidation

The experimental set-up for the oxidation of this aged raw landfill leachate is shown in Figure 3.1. Extra dry oxygen gas was delivered to the ozone generator (Welsbach Corporation, Model: T-816) at pressure of 103.5 kPa. The ozone concentration in the feed gas of the first gas washing bottle was 42 mg O_3/L, which was determined by the following procedure: feed gas was absorbed with 250 mL of 2% potassium iodide (KI) solution in the first gas washing bottle, and 400 mL of 2% KI solution in the second and the third gas washing bottles, respectively. The volume of the off-gas from the third gas washing bottle was measured with a wet test meter (GCA/Precision Scientific, Chicago, IL, USA). When the reading of the wet test meter was about 6.0 L, the calibration process was stopped, then the ozonated KI solution was transferred into a 1-L Erlenmeyer flask, and titrated with 0.5 N sodium thiosulfate ($Na_2S_2O_3$) standard solution after being acidified with 0.5 mL concentrated sulphuric acid (H_2SO_4). After the ozone generator was calibrated, 250 mL of the aged raw landfill leachate (pH = 8.30, temperature = 22°C for both O_3 only and O_3/H_2O_2) was put into the first gas washing bottle, ozone in the off-gas was captured with 400 mL of 2% KI solution in the second and the third gas washing bottles, respectively.

When the KI solution in the second gas washing bottle became brown, the off-gas from the first gas washing bottle was switched to the parallel gas washing bottle so that the ozonated KI solution could be transferred into the 4-L Erlenmeyer flask and then the gas washing bottle could be refilled with 2% KI solution again. In this way, the ozone concentration in the off-gas was determined, and the used-ozone doses could be estimated.

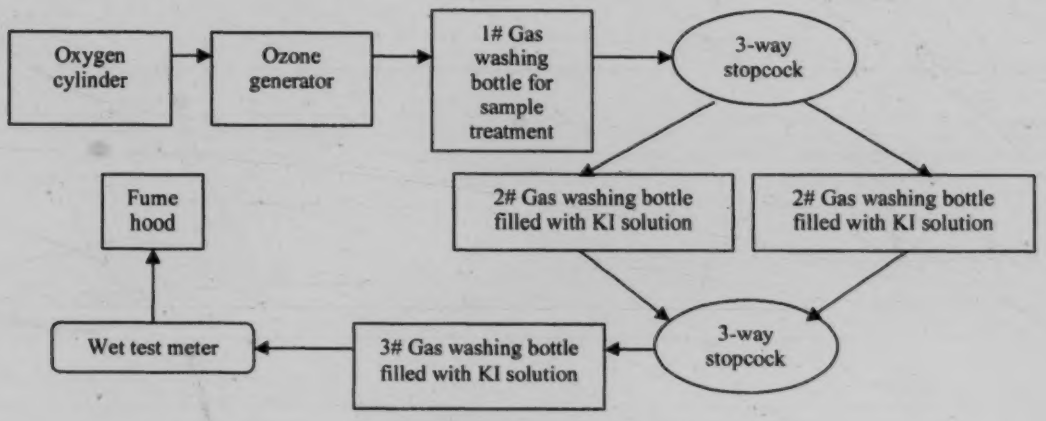
Oxygen cylinder
Ozone generator
1# Gas washing bottle for sample treatment
3-way stopcock
Fume hood
2# Gas washing bottle filled with KI solution
2# Gas washing bottle filled with KI solution
Wet test meter
3# Gas washing bottle filled with KI solution
3-way stopcock

Figure 3.1 Schematic diagram of set-up for leachate oxidation with O_3 only and O_3/H_2O_2.

3.2.3 Conditions for leachate oxidation

Figure 3.2 shows the effect of pH, H_2O_2 dose and contact time before ozonation on COD. When the leachate pH was lowered to 4.0 before adding H_2O_2, the lowered pH caused severe problems for O_3 to dissolve in the leachate, and resulted in very low used-ozone doses even though the applied O_3 doses for samples 2 to 5 were the same. On the contrary, pH = 8.3 (unadjusted pH) gave better COD reduction. Moreover, higher H_2O_2 dose and longer contact time before ozonation did not show pronounced advantages in terms of COD reduction.

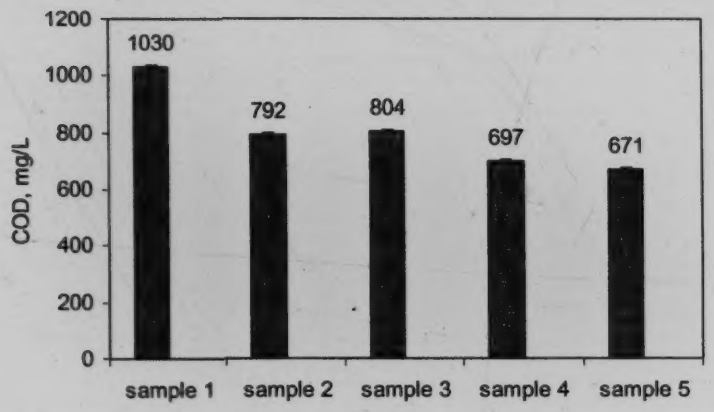

Figure 3.2 Effect of pH, H_2O_2 dose and contact time before ozonation on COD.

Sample 1: pH = 8.3, aged raw leachate before oxidation;

Sample 2: pH = 4.0, (0.46 g O_3 + 0.63 g H_2O_2)/L leachate, contact time = 0 h;

Sample 3: pH = 4.0, (0.42 g O_3 + 0.63 g H_2O_2)/L leachate, contact time = 2 h;

Sample 4: pH = 8.3, (1.04 g O_3 + 0.63 g H_2O_2)/L leachate, contact time = 2 h;

Sample 5: pH = 8.3, (1.01 g O_3 + 1.26 g H_2O_2)/L leachate, contact time = 24 h.

Figure 3.3 shows the effect of treatment temperature on the COD reduction. The used-ozone dose increased at the temperature of 4°C and higher H_2O_2 dose. However, the higher used-ozone dose did not make obvious positive contribution to the COD reduction since at the lower temperature, the reaction kinetics of ozone with organic compounds were also low.

Therefore, the conditions for the leachate oxidation were set at temperature = 22°C, pH = 8.3, H_2O_2 dose of 0.63 g H_2O_2/L leachate, and H_2O_2 added right before ozonation (i.e., contact time was 0 h).

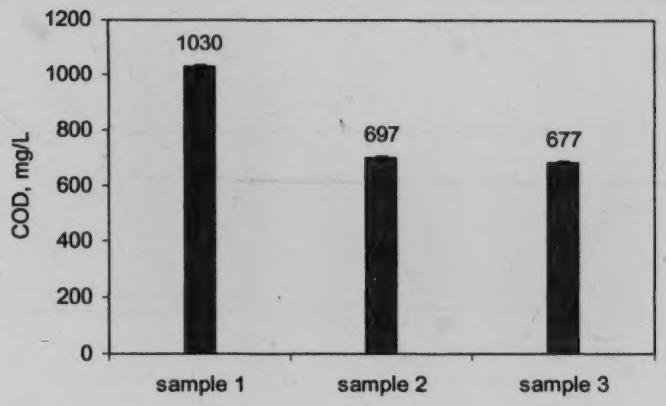

Figure 3.3 Effect of treatment temperature on COD.

Sample 1: Aged raw leachate before oxidation;

Sample 2: T = 22°C, (1.04 g O_3 + 0.63 g H_2O_2)/L leachate, contact time = 2 h;

Sample 3: T = 4°C, (2.02 g O_3 + 1.26 g H_2O_2)/L leachate, contact time = 0 h.

3.2.4 Analytical methods

3.2.4.1 COD, BOD_5, colour, NH_3-N, alkalinity and nitrite+nitrate

COD, BOD_5, colour, NH_3-N, alkalinity and nitrite+nitrate were determined following the Standard Methods (American Public Health Association et al. 1998). COD was analyzed in triplicate, BOD_5, colour, NH_3-N, alkalinity were measured in duplicate. Nitrite+nitrate analysis was performed by using flow injection analyzer (FIA, Pulse Instrumentation Ltd., Saskatoon, Saskatchewan, Canada, pump model 9211004) in the Limnology Laboratory, Department of Biological Sciences, University of Alberta.

3.2.4.2 Sample pretreatment for the molecular size distribution analysis

After oxidation all of the samples were purged with extra dry helium for 15 min to remove ozone residue. For the samples oxidized with O_3/H_2O_2, after being purged with

helium for 15 min, 1.0 mL of Bovine liver catalase (Sigma-Aldrich Canada, catalogue #: C1345, nominal molecular size 250,000 Dalton) solution at 1 mg catalase/mL was added into the sample to destroy the H_2O_2 residue so that the influence of H_2O_2 residue on COD and BOD_5 was eliminated. Meanwhile, the COD and BOD_5 of the Bovine liver catalase solution were also tested together with the samples to correct for the positive errors of COD and BOD_5 caused by the catalase addition.

Before injection, samples of before oxidation and after oxidation with O_3 only were filtered by using Millipore Millex nonsterile syringe filters with 0.45 μm pore size PVDF membrane (Fisher Scientific Canada, catalogue #: SLHV013NL) to remove the particles from the samples. To eliminate the fatal influence of Bovine liver catalase on the gel filtration column, the samples oxidized with O_3/H_2O_2 were centrifuged by using Ultrafree®-CL high-flow Biomax-PB centrifugal filter units (Sigma-Aldrich Canada, catalogue #: M2286) with 100,000 Dalton nominal molecular weight limit (NMWL) PTHK polyethersulfone membrane. The centrifuge was run at 3,000 rpm for 10 min.

3.2.4.3 Methodology development for molecular size distribution analysis

3.2.4.3.1 NaCl concentration in eluant

Molecular size distribution analysis was performed with HPLC (Shimadzu Corporation, Japan) equipped with PW_{XL} guard column (Supelco/Sigma-Aldrich Canada, catalogue #: 808033, 40 mm × 6.0 mm, 12 μm particle size), $G3000PW_{XL}$ gel filtration column (Supelco/Sigma-Aldrich Canada, catalogue #: 808021, 300 mm × 7.8 mm, 6 μm particle size), and UV detector at 254 nm. 100 μL of particle-free (filtered with 0.45 μm pore size PVDF membrane (Fisher Scientific Canada, catalogue #: SLHV013NL)) sample

was manually injected into the 20-μL sampling loop. The data acquisition system for the HPLC was Shimadzu Class-VP.

The molecular size distribution analysis was performed to observe the change of the large refractory organic compounds and the formation of small molecules after advanced oxidation. Therefore, the HPLC was set up in terms of the performance of separation of the small molecules. The sample of <1,000 Dalton was used to set up the HPLC operating condition.

The most important factor that can affect the separation of landfill leachate with gel filtration column is the electrolyte concentration in the eluant (Ceccanti et al. 1989; Lecoupannec 1999). Therefore, the molecular size distributions of the sample of <1,000 Dalton were analyzed by using 2 mM, 5 mM, 10 mM and 20 mM sodium chloride (NaCl) solutions as eluants, flow rate was 0.5 mL/min, and the UV detector was set at 254 nm. It was found that both 10 mM NaCl and 5 mM NaCl solutions gave good separation for the molecular size distribution analysis of the sample of <1,000 Dalton (Figure 3.4), and the best separation was achieved by using the 10 mM NaCl solution. On the molecular size distribution chromatograms in this thesis, the AUFS means UV absorbance unit full scale.

3.2.4.3.2 Sample pH

Another important factor that can affect the separation of the landfill leachate with gel filtration column is the pH of the samples (Kipton et al. 1992). The HPLC operating condition was set at 10 mM NaCl as eluant, flow rate of 0.5 mL/min, the molecular size distribution of the aged raw leachate at pH of 8.3, 7.0, 6.5, 6.0, 5.0, 4.5 and 4.0 were analyzed. The results are shown in Figure 3.5. The pH affected the first three peaks, but did not have salient influence on the fourth peak.

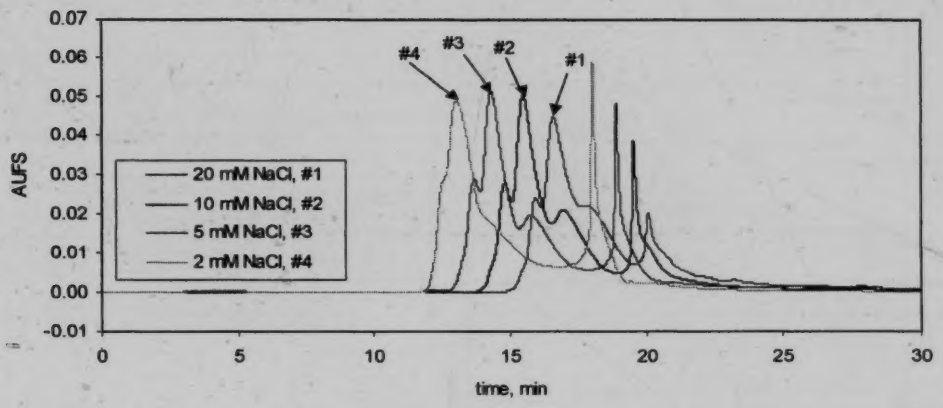

Figure 3.4 Molecular size distribution of the sample of <1,000 Dalton (pH = 8.29, unadjusted) versus NaCl concentrations.

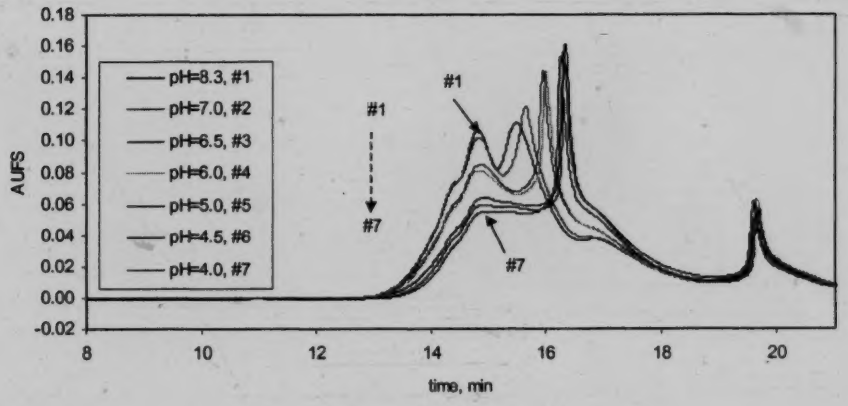

Figure 3.5 Molecular size distribution of the aged raw leachate versus pH.

3.2.4.3.3 Unstable intermediate oxidation by-products

For the samples of the aged raw leachates after oxidation with either O_3 only or O_3/H_2O_2, the unstable oxidation by-products were observed. Therefore, such unstable intermediate oxidation by-products versus time after oxidation were monitored, and the results are shown in Figures 3.6 and 3.7 for O_3 only and Figures 3.8 and 3.9 for O_3/H_2O_2.

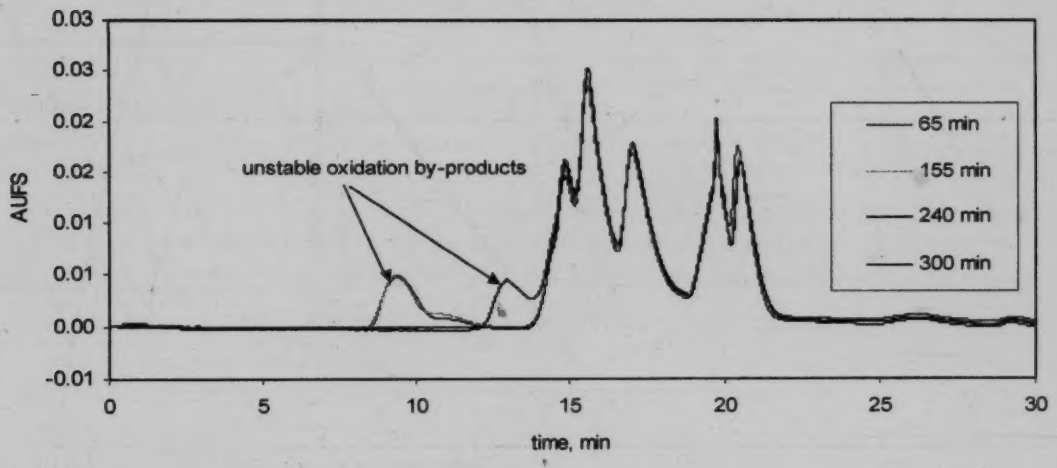

Figure 3.6 Unstable oxidation by-products of O_3 only versus time (t < 300 min).

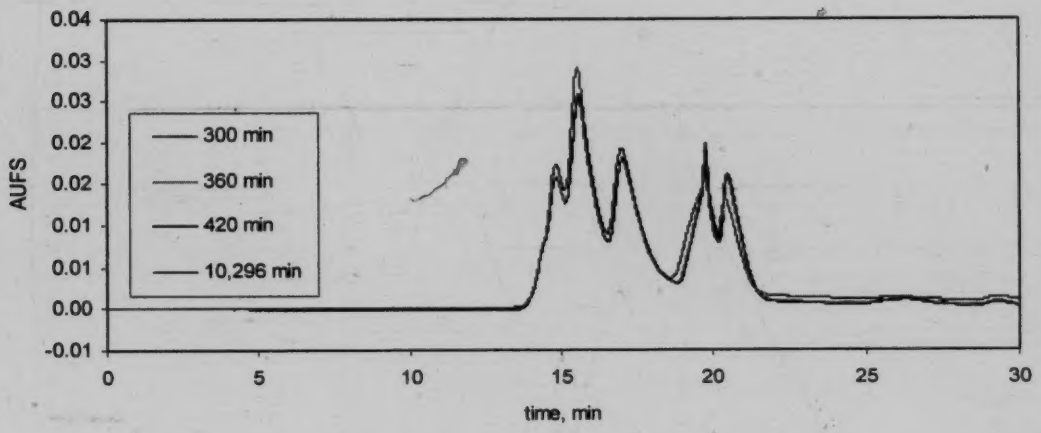

Figure 3.7 Molecular size distribution of O_3 only after stabilization versus time (t > 300 min).

Figures 3.6 to 3.9 demonstrate that the aged raw leachate after oxidation with O_3 only took 300 min to become stabilized, while the aged raw leachate after oxidation with

O_3/H_2O_2 took 150 min to become stabilized. Therefore, the molecular size distributions of all the samples after oxidation with O_3 only and O_3/H_2O_2 were analyzed within 5 to 24 hours and 3 to 24 hours, respectively.

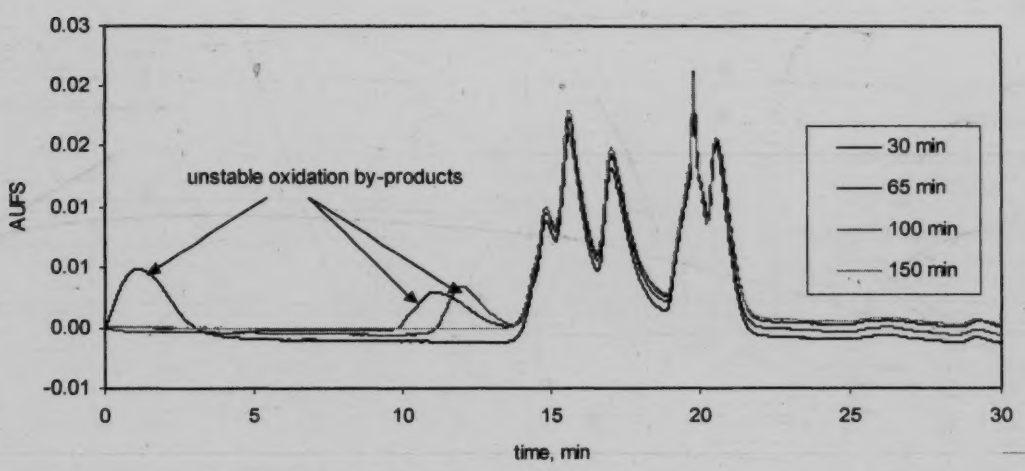

Figure 3.8 Unstable oxidation by-products of O_3/H_2O_2 versus time ($t < 150$ min).

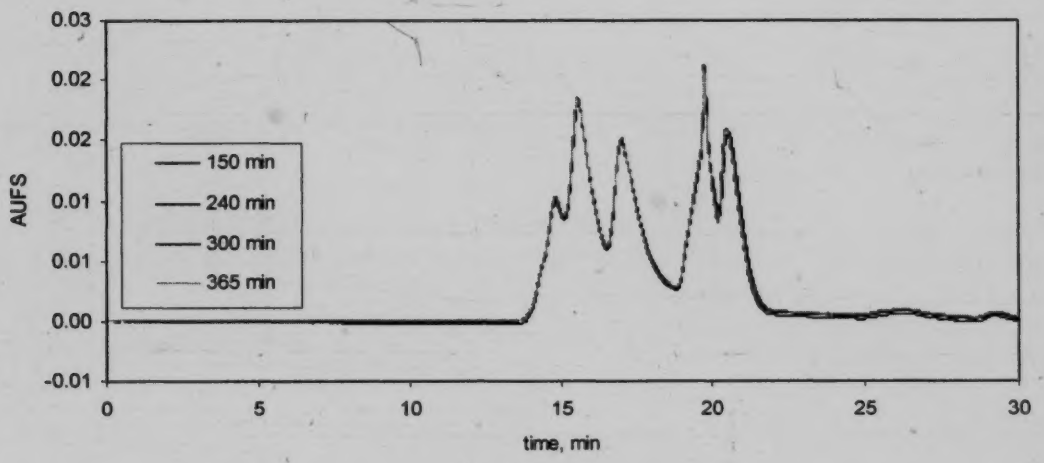

Figure 3.9 Molecular size distribution of O_3/H_2O_2 after stabilization versus time ($t > 150$ min).

3.2.4.3.4 Calibration of the G3000PW$_{XL}$ column

Since the HPLC operating condition was set up with 10 mM NaCl as eluant, and the UV detector set at 254 nm, the size standards for the column G3000PW$_{XL}$ had to be dissolved in the chosen eluant. Therefore, Fluka® polyethylene glycol standards at molecular weights of 200; 300; 600; 1,000; 2,000; 4,000; 6,000; 8,000; 12,000 and 20,000 Dalton (Sigma-Aldrich Canada, catalogue #s: 81282, 81283, 81286, 81288, 81290, 81292, 81293, 81294, 81296 and 81298, respectively) and ethylene glycol (Fisher Scientific Canada, catalogue #: E178-500, molecular weight: 62 Dalton) were selected as the size standards for the G3000PW$_{XL}$ column.

The concentration of all the standard solution was 20 mg/mL. The standard solutions were filtered with Millipore Millex nonsterile syringe filters with 0.45 μm pore size PVDF membrane (Fisher Scientific Canada, catalogue #: SLHV013NL) before injection. Figure 3.10 is the standard curve for the G3000PW$_{XL}$ column.

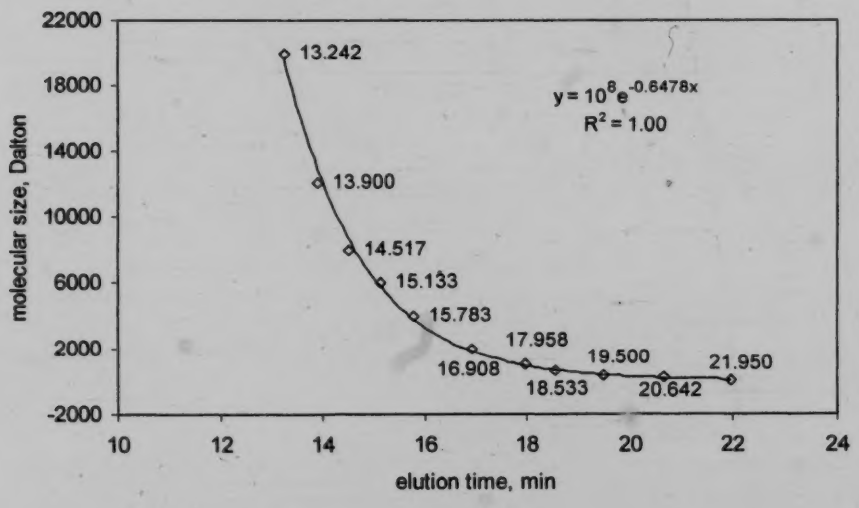

Figure 3.10 Standard curve for molecular size distribution with G3000PW$_{XL}$ column.

3.3 Results and discussion

3.3.1 Chemical oxygen demand (COD)

Figure 3.11 shows the COD of the aged raw landfill leachate after oxidation with O_3 only and O_3/H_2O_2 as a function of the used-ozone dose. The COD of the aged raw landfill leachate, during O_3 only and O_3/H_2O_2 treatments, decreased with the increase of the used-ozone dose. The regression models on the COD after oxidation versus the used-ozone dose for the both treatments are shown in Table 3.2.

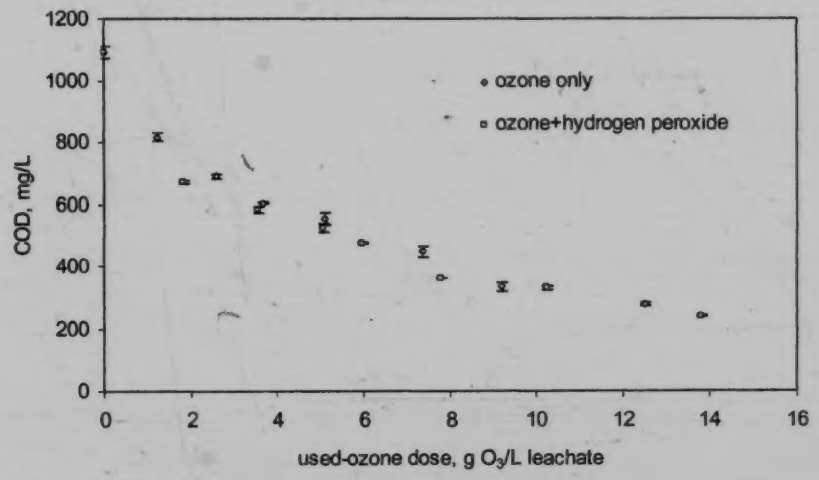

Figure 3.11 COD versus used-ozone dose.

The addition of H_2O_2 marginally enhanced COD reduction at lower used-ozone doses. However, the difference between CODs of O_3 only and O_3/H_2O_2 became smaller as the used-ozone dose increased because increased COD reduction resulting from the addition of H_2O_2 being compensated by the ozone applied subsequently. At the used-ozone dose 2.6 g O_3/L leachate for O_3 only and 3.6 g O_3/L leachate for O_3/H_2O_2, COD removal

efficiency was 37% for O_3 only and 47% for O_3/H_2O_2. The best COD removal efficiency of 75% for O_3 only and 78% for O_3/H_2O_2 was achieved when the used-ozone dose of 12.5 g O_3/L leachate for O_3 only and 13.8 g O_3/L leachate for O_3/H_2O_2.

Table 3.2 Summary of the treatment efficiency models (x = used-ozone dose, g O_3/L leachate).

Parameter	Process	Model	R^2	Others
y = COD, mg/L	O_3 only	$y = 1{,}090 \times e^{-0.122x}$	0.90	1,090 = COD before
	O_3/H_2O_2	$y = 1{,}090 \times e^{-0.124x}$	0.77	oxidation, mg/L.
	Pooled	$y = 1{,}090 \times e^{-0.123x}$	0.85	
y = BOD_5/COD	O_3 only	$y = 4.7 \times 10^{-2}\ln(x) + 9.2 \times 10^{-2}$	0.98	
	O_3/H_2O_2	$y = 4.3 \times 10^{-2}\ln(x) + 8.9 \times 10^{-2}$	0.91	
	Pooled	$y = 4.4 \times 10^{-2}\ln(x) + 9.1 \times 10^{-2}$	0.93	
y = NH_3-N, mg N/L	O_3 only	$y = 455 - 24.7x$	0.98	455 = NH_3-N before
	O_3/H_2O_2	$y = 455 - 24.5x$	0.95	oxidation, mg N/L.
	Pooled	$y = 455 - 24.6x$	0.96	
y = nitrite+nitrate, mg N/L	O_3 only	$y = 24.2x$	0.98	
y = alkalinity,	O_3 only	$y = 4{,}030 - 232x$	0.95	4,030 = alkalinity before
mg/L as $CaCO_3$	O_3/H_2O_2	$y = 4{,}030 - 185x$	0.95	oxidation, mg/L as
	Pooled	$y = 4{,}030 - 206x$	0.90	$CaCO_3$.

As mentioned before, the major components of the aged raw leachate are humic substances including humic acids and fulvic acids (Chian 1977; Lecoupannec 1999) with molecular weight within 1,000 to 10,000 Dalton. Humic substances consist of a skeleton of alkyl/aromatic units cross-linked mainly by oxygen and nitrogen groups with the major functional groups being carboxylic acid, phenolic and alcoholic hydroxyls, ketone and quinone groups (Livens 1991; Schulten et al. 1991). Fulvic acids are richer in carboxylic acid, phenolic and ketonic groups (Schulten and Schnitzer, 1995). Compared to humic acids, the structures of fulvic acids are more aliphatic and less aromatic. Humic substances

are not easily oxidized completely. Therefore, the COD of the aged raw leachate after being oxidized with either O_3 only or O_3/H_2O_2 at different used-ozone doses follows an exponential decay function. The similar relationship between COD after oxidation and used-ozone dose has been proposed by Gamal El-Din and Smith (2002) and Zhou and Smith (2000).

3.3.2 Five-day biochemical oxygen demand (BOD_5)

Figure 3.12 depicts the change in BOD_5 as a function of the used-ozone dose. In general, BOD_5 increased after oxidation in both treatments, BOD_5 had the same increase and decrease trends. The values of BOD_5 after oxidation with O_3 only were always higher than those after oxidation with O_3/H_2O_2 at lower used-ozone doses. The highest BOD_5 value also occurred at the used-ozone dose of 2.6 g O_3/L leachate and 3.6 g O_3/L leachate for both O_3 only and O_3/H_2O_2 treatments; i.e., when the aged raw landfill leachate was ozonated for 30 min. After the highest value point, BOD_5 decreased with the increase of used-ozone doses. This trend is in accordance with the results of Karrer et al. (1997).

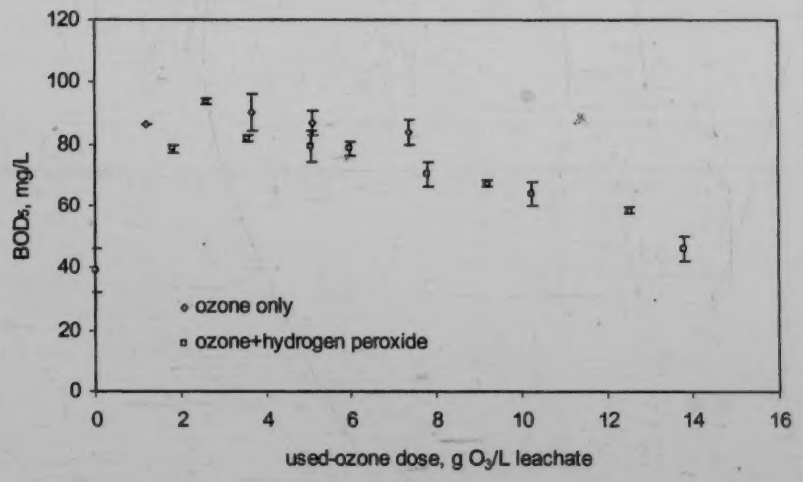

Figure 3.12 BOD_5 versus used-ozone dose.

3.3.3 Ratio of BOD_5/COD

Figure 3.13 presents the relationship between the ratio of BOD_5/COD and the used-ozone dose for both treatments, and the regression equations are shown in Table 3.2.

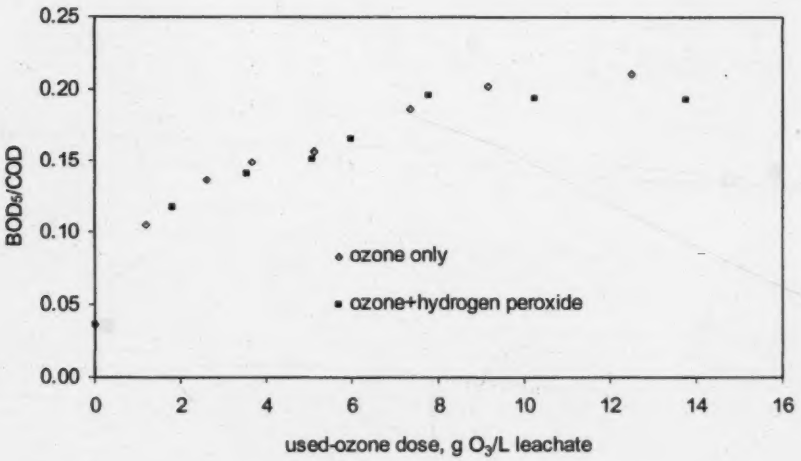

Figure 3.13 BOD_5/COD versus used-ozone dose.

After O_3 oxidation and O_3/H_2O_2 oxidation, the increased BOD_5 and decreased COD ended up with the improved ratio of BOD_5/COD, which indicates that the biodegradability of leachate has been improved by the oxidation with O_3 only or O_3/H_2O_2. When the used-ozone dose was 2.6 g O_3/L leachate for O_3 only and 3.6 g O_3/L leachate for O_3/H_2O_2, the ratio of BOD_5/COD was 0.136 and 0.140, respectively. This means the aged raw leachate became biodegradable after oxidation with O_3 only or O_3/H_2O_2, and it can be recycled back to the RBC unit.

3.3.4 Colour

Figure 3.14 shows that the colour can be reduced effectively with either O_3 only or

O_3/H_2O_2. At the used-ozone dose of 1.2 g O_3/L leachate for O_3 only and 1.8 g O_3/L leachate for O_3/H_2O_2, colour removal efficiency was 90% for both treatments. With the increase of used-ozone dose, the colour removal efficiency slightly increased, and the best colour removal efficiency, 96% for O_3 only and 97% for O_3/H_2O_2, was achieved at used-ozone dose of 7.4 g O_3/L leachate for O_3 only and 7.8 g O_3/L leachate for O_3/H_2O_2.

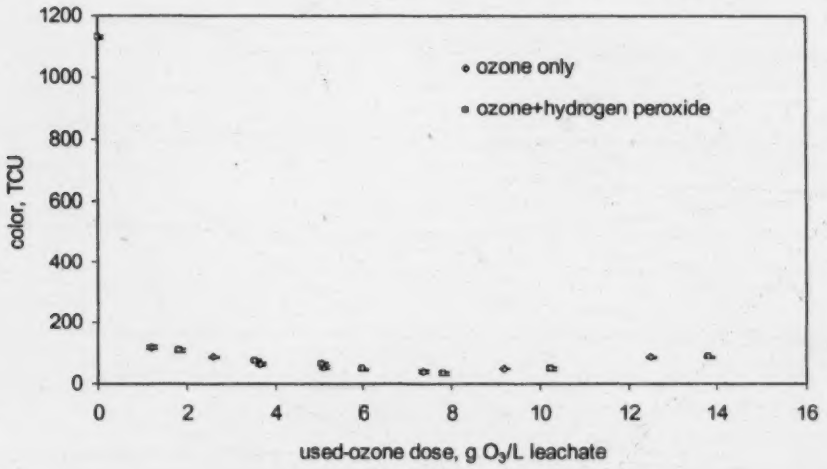

Figure 3.14 Colour versus used-ozone dose.

The chromophores in the humic substances causing yellow colour and brown colour include quinonoid structure (Gore et al. 1962) and/or azo structure (Hao et al. 2000). These functional groups contain either benzene rings or nitrogen-to-nitrogen double bonds, or both. These structures are very vulnerable on the attack of molecular ozone (Bailey and Trahanovsky, 1978) or •OH radicals. Once such structures are destroyed, colour will disappear. In addition, the colour for both O_3 only and O_3/H_2O_2 increased again when the used-ozone dose was greater than 7.8 g O_3/L leachate, which might be due to the oxidation by-products which have other colour-causing functional groups.

3.3.5 Ammonia-nitrogen (NH_3-N)

Figure 3.15 presents the NH_3-N and nitrite+nitrate changes with the increase of the used-ozone dose. The regression models describing the relationship between NH_3-N and used-ozone dose for both treatments are shown in Table 3.2. Since the NH_3-N decrease rates for O_3 only and O_3/H_2O_2 were almost identical, it was hypothesized that the NH_3-N takes the same reaction pathway during the oxidation with O_3 only or O_3/H_2O_2. To verify the reaction pathway of NH_3-N during the oxidation with O_3 only and O_3/H_2O_2, nitrite+nitrate in the leachate samples after oxidation with O_3 only was analyzed. It was found that the nitrite+nitrate also linearly increased with used-ozone dose (Table 3.2). Therefore, NH_3-N was oxidized by O_3 only or O_3/H_2O_2 and formed nitrite and nitrate. It was also found that the sum of NH_3-N and nitrite+nitrate was constant within the tested range of the used-ozone doses.

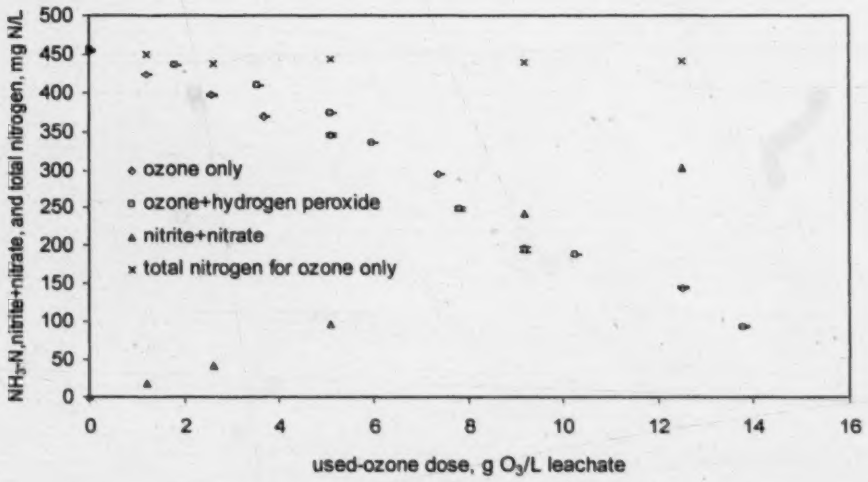

Figure 3.15 NH_3-N, nitrite+nitrate and total nitrogen versus used-ozone dose.

Singer and Zilli (1975) reported that NH_3-N was oxidized by ozone to nitrate in wastewater. Haag et al. (1984) drew the same conclusion for the ozonation of NH_3-N in water containing bromide (Br^-) bicarbonate (HCO_3^-) and phosphate buffer. To date, there is little information available about how the NH_3-N in landfill leachate behaves during the oxidation with O_3 only and O_3/H_2O_2. Bigot et al. (1994) reported that ammonia was not affected by oxidation with O_3 only and O_3/H_2O_2. In their research, the small NH_3-N change at lower used-ozone dose might be considered as experimental error. Karrer et al. (1997) nitrified NH_3-N with a fluidized sand biofilm reactor to avoid the reaction of ozone with ammonia. Therefore, the results of this research verified that the NH_3-N was oxidized to nitrate.

Usually, NH_3-N concentration of aged raw leachate is still high; therefore, it has to be determined through economic analysis whether NH_3-N should be removed by pH adjustment and air stripping before oxidation or not. Moreover, the influence of nitrite and nitrate on the subsequent biological treatment system or the receiving watercourses should be considered.

3.3.6 Alkalinity

Figure 3.16 depicts the alkalinity change with the increase of the used-ozone dose. The regression models on alkalinity and used-ozone dose for both treatments are also summarized in Table 3.2. The initial pH of this leachate before oxidation was 8.30, which indicated that the major alkalinity component was bicarbonate (HCO_3^-). At the used-ozone dose of 12.5 g O_3/L leachate, the alkalinity decreased 2,900 mg $CaCO_3$/L (From Table 3.2, the alkalinity after ozonated at 12.5 g O_3/L leachate was 2,900 mg $CaCO_3$/L ($232 \times 12.5 =$ 2,900 mg $CaCO_3$/L). In the process of oxidation with O_3 only, NH_3-N was oxidized to

nitrate (NO_3^-). At the used-ozone dose of 12.5 g O_3/L leachate the amount of NH_3 oxidized to NO_3^- was 309 mg N/L (From Table 3.2, at used-ozone dose of 12.5 g O_3/L leachate, NH_3-N after ozonation was 24.7 × 12.5 = 309 mg N/L).

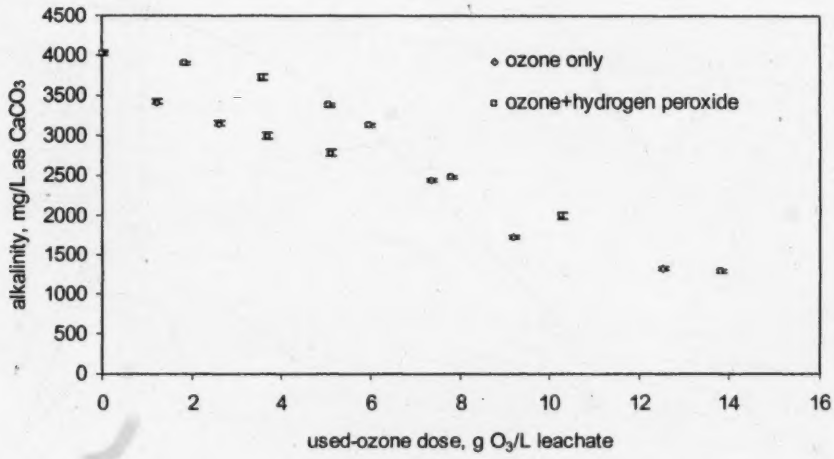

Figure 3.16 Alkalinity versus used-ozone dose.

$NH_3 + 4O_3 \rightarrow NO_3^- + 4O_2 + H_2O + H^+$ (Singer and Zilli 1975; Haag et al. 1984)

14 mg N/L 1 mM

309 mg N/L *a*

So, *a* = (309 mg N/L)/(14 mg N/L) × 1 mM = 22 mM.

$HCO_3^- + H^+ \rightarrow CO_2\uparrow + H_2O$

100 mg $CaCO_3$/L 1 mM

b 22 mM

Therefore, *b* = (100 mg $CaCO_3$/L × 22 mM)/(1 mM) = 2,200 mg $CaCO_3$/L. That suggests that the H^+ resulting from NH_3-N oxidation could account for 76% [(2,200 mg

$CaCO_3$/L)/(2,900 mg $CaCO_3$/L) = 76%] of the alkalinity loss. Moreover, carboxylic acids formed by the O_3 only oxidation of humic substances might also reduce the alkalinity.

3.3.7 Pooled regression models

Statistically, the difference between COD, ratio of BOD_5/COD, NH_3-N, and alkalinity of O_3 only and O_3/H_2O_2 treatments was not significant at a 95% confidence level by using t-test to compare two linear models (Zar 1999). Therefore, the data of each parameter from both treatments were pooled together and the regression models for both treatments were developed (see Table 3.2).

As far as the models are considered, it seems to suggest that the simple and known reactions, such as reactions happened to alkalinity and NH_3-N, ended up with the linear models; whereas, the complicated and unknown reactions, such as reactions happened to COD and BOD_5, resulted in the nonlinear models.

3.3.8 Molecular size distribution

Figure 3.17 and Figure 3.18 present the molecular size distributions of the aged raw leachate before oxidation and after oxidation at different used-ozone doses without H_2O_2 addition and with addition of H_2O_2 at 0.63 g H_2O_2/L leachate, respectively. The molecular weight of each peak was determined based on its elution time and the standard curve for molecular size distribution of G3000PW_{XL} column (Figure 3.10). Figures 3.17 and 3.18 show that the peaks in the aged raw leachate with molecular weights of 6,840; 4,270; 1,680 and 287 Dalton were reduced by O_3 only and O_3/H_2O_2 oxidation. With the increase of the used-ozone dose, the peaks with molecular weights larger than 1,680 Dalton became increasingly smaller; while, the peak with molecular weight of 287 Dalton did not change very much. Meanwhile, the oxidation by-products shown as the peak at 20.556 min

(molecular weight 165 Dalton) and the toe berm on the left of the peak at 19.700 min (molecular weight 287 Dalton) increased with the increase of the used-ozone dose.

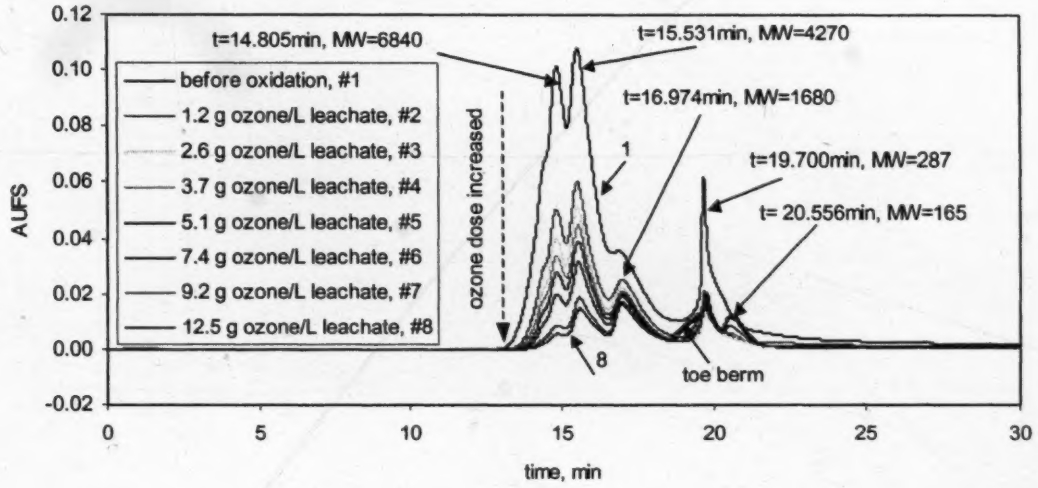

Figure 3.17 Molecular size distributions versus used-ozone dose without H_2O_2 addition (treatment temperature = 22°C, initial pH = 8.30).

Figures 3.19 to 3.25 present the molecular size distributions of the aged raw leachate before and after oxidation with O_3 only and O_3/H_2O_2 at the same applied-ozone dose though the associated used-ozone doses differ.

1) The addition of H_2O_2 at the dose of 0.63 g H_2O_2/L leachate enhanced the reduction of the peaks with molecular weights of 6,840; 4,270; and 1,680 Dalton at the lower used-ozone doses. However, the effect of the addition of H_2O_2 became less obvious when the used-ozone dose was greater than 9.2 g O_3/L leachate for O_3 only and 10.3 g O_3/L leachate for O_3/H_2O_2. These results are in accordance with the COD values after oxidation with O_3 only and O_3/H_2O_2 (Figure 3.11).

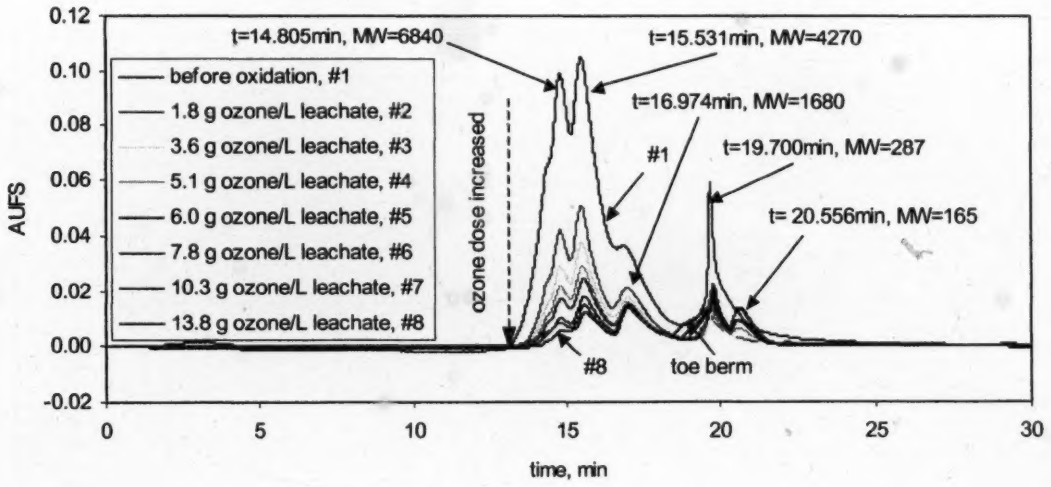

Figure 3.18 Molecular size distributions versus used-ozone dose with H_2O_2 addition at 0.63 g H_2O_2/L leachate (treatment temperature = 22°C, initial pH = 8.30).

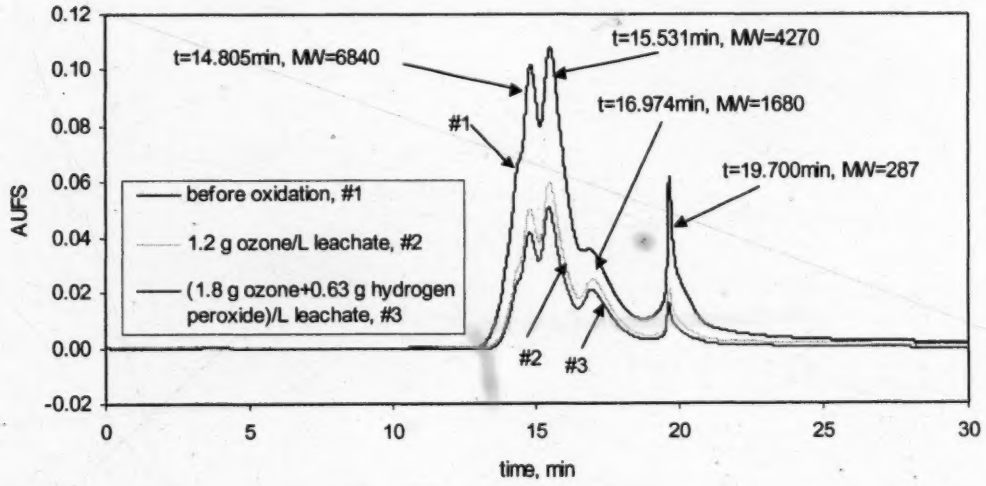

Figure 3.19 Molecular size distributions for used-ozone dose of 1.2 g O_3/L leachate for O_3 only and 1.8 g O_3/L leachate for O_3/H_2O_2 (treatment temperature = 22°C, initial pH = 8.30, applied-ozone dose was 7.6 g O_3/L leachate).

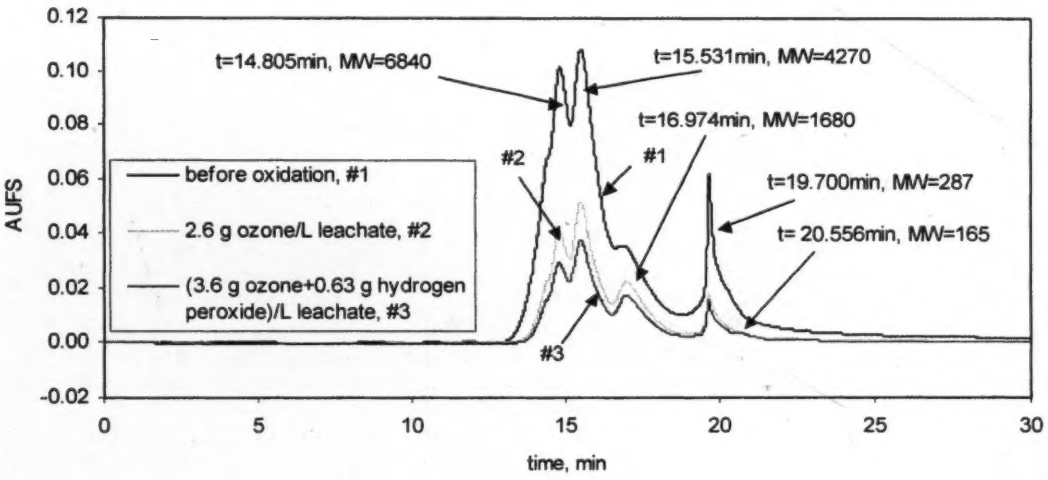

Figure 3.20 Molecular size distributions for used-ozone dose of 2.6 g O_3/L leachate for O_3 only and 3.6 g O_3/L leachate for O_3/H_2O_2 (treatment temperature = 22°C, initial pH = 8.30, applied-ozone dose was 15.2 g O_3/L leachate).

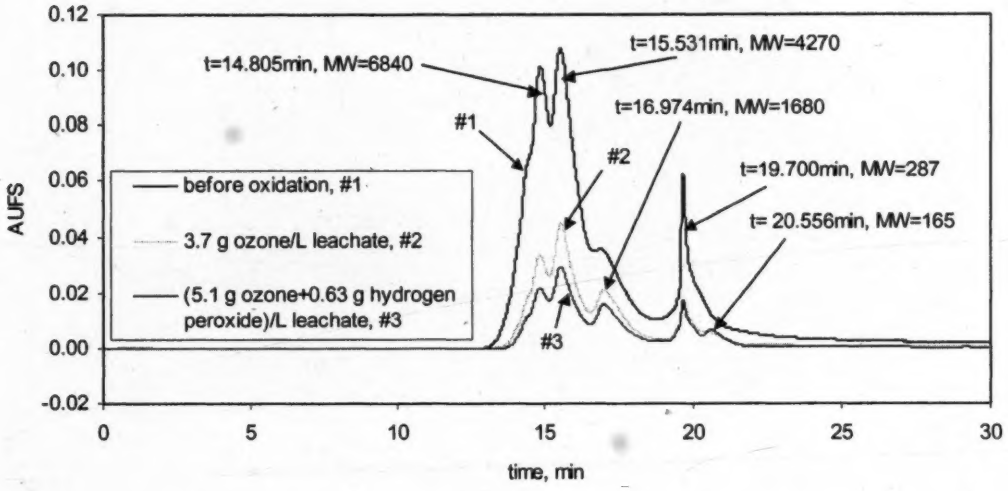

Figure 3.21 Molecular size distributions for used-ozone dose of 3.7 g O_3/L leachate for O_3 only and 5.1 g O_3/L leachate for O_3/H_2O_2 (treatment temperature = 22°C, initial pH = 8.30, applied-ozone dose was 22.7 g O_3/L leachate).

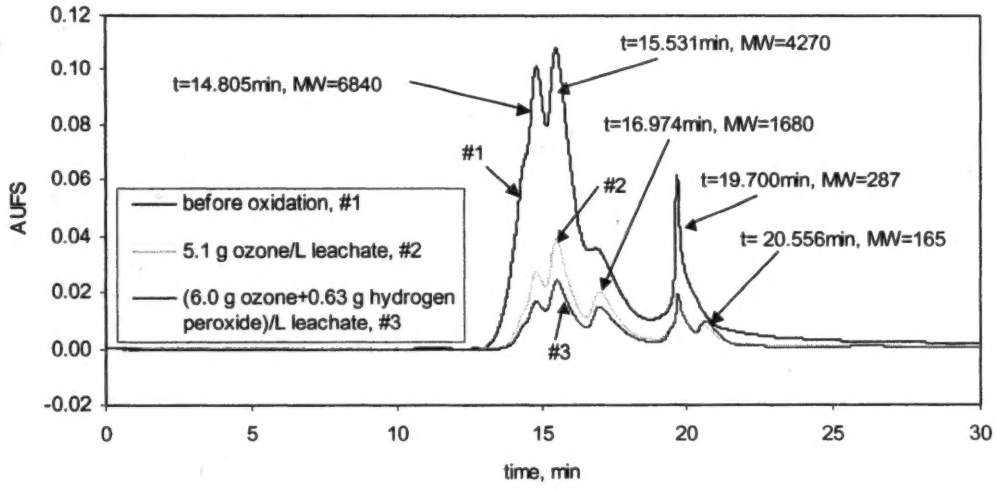

Figure 3.22 Molecular size distributions for used-ozone dose of 5.1 g O_3/L leachate for O_3 only and 6.0 g O_3/L leachate for O_3/H_2O_2 (treatment temperature = 22°C, initial pH = 8.30 applied-ozone dose was 30.3 g O_3/L leachate).

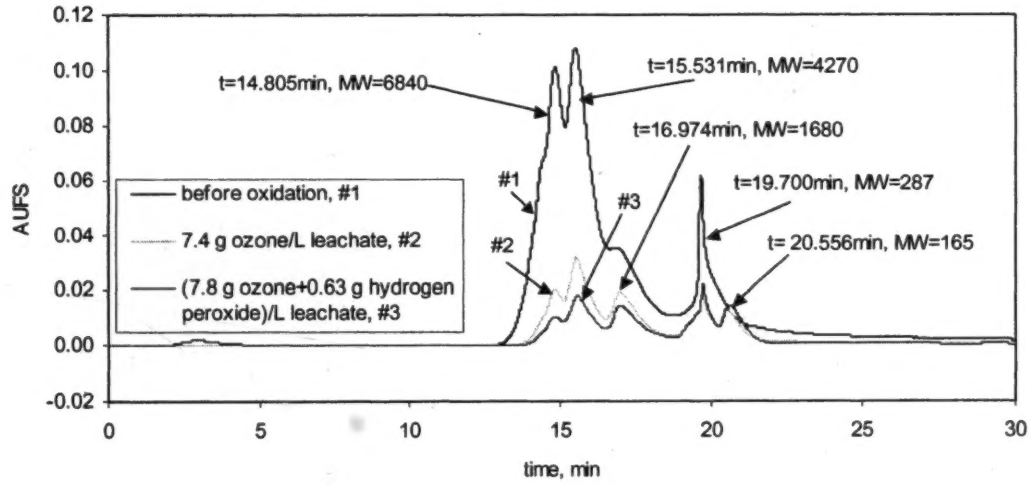

Figure 3.23 Molecular size distributions for used-ozone dose of 7.4 g O_3/L leachate for O_3 only and 7.8 g O_3/L leachate for O_3/H_2O_2 (treatment temperature = 22°C, initial pH = 8.30, applied-ozone dose was 45.4 g O_3/L leachate).

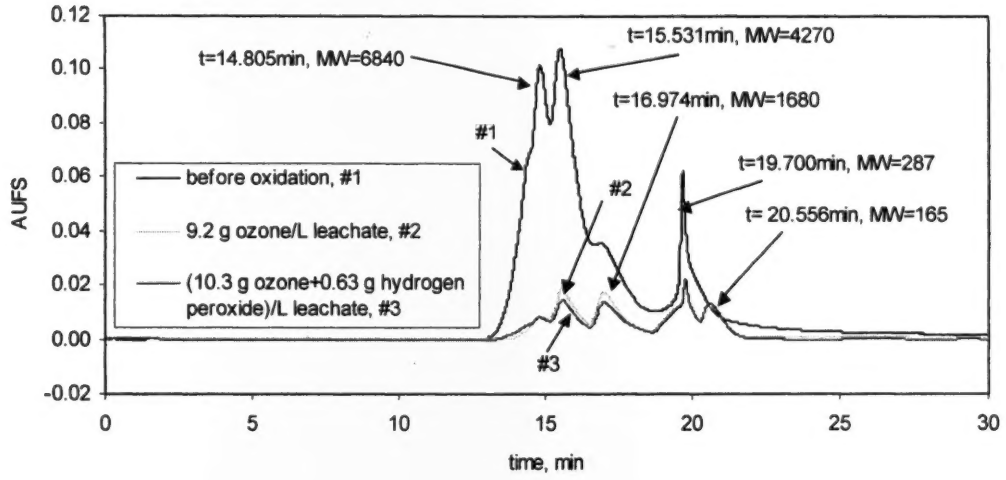

Figure 3.24 Molecular size distributions for used-ozone dose of 9.2 g O_3/L leachate for O_3 only and 10.3 g O_3/L leachate for O_3/H_2O_2 (treatment temperature = 22°C, initial pH = 8.30, applied-ozone dose was 60.5 g O_3/L leachate).

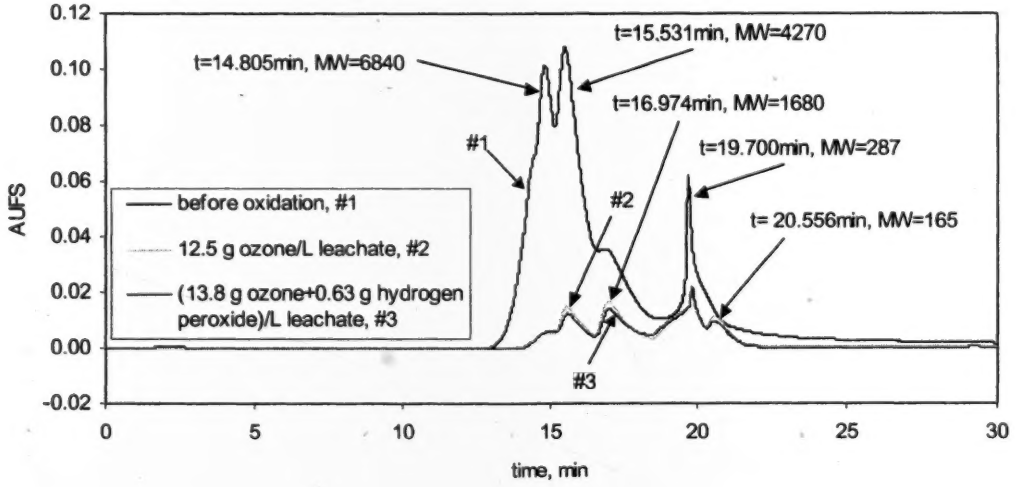

Figure 3.25 Molecular size distributions for used-ozone dose of 12.5 g O_3/L leachate for O_3 only and 13.8 g O_3/L leachate for O_3/H_2O_2 (treatment temperature = 22°C, initial pH = 8.30, applied-ozone dose was 92.2 g O_3/L leachate).

2) For the peak with molecular weight of 287 Dalton, it shows different scenarios at different used-ozone doses.

   a) At the used-ozone doses of 1.2 g O_3/L leachate and 2.6 g O_3/L leachate for O_3 only and 1.8 g O_3/L leachate and 3.6 g O_3/L leachate for O_3/H_2O_2 (Figures 3.19 and 3.20), this peak for O_3 only was bigger than that for O_3/H_2O_2.

   b) At the used-ozone dose of 3.7 g O_3/L leachate for O_3 only and 5.1 g O_3/L leachate for O_3/H_2O_2 (Figure 3.21), this peak of O_3 only was almost the same as that of O_3/H_2O_2 oxidation.

   c) At the used-ozone dose from 5.1 to 12.5 g O_3/L leachate for O_3 only and from 6.0 to 13.8 g O_3/L leachate for O_3/H_2O_2 (Figures 3.22 to 3.25), this peak of O_3 only was smaller than that of O_3/H_2O_2 oxidation.

   Therefore, these results probably suggest that at the used-ozone dose from 1.2 to 2.6 g O_3/L leachate for O_3 only and from 1.8 to 3.6 g O_3/L leachate for O_3/H_2O_2, this peak was the leftover of the peak with molecular weight of 287 Dalton of the aged raw leachate; at the used-ozone dose from 3.7 to 12.8 g O_3/L leachate for O_3 only and from 5.1 to 13.8 g O_3/L leachate for O_3/H_2O_2, this peak may also include the oxidation products of the large molecules, whose molecular weights were also 287 Dalton.

3) For the new peak eluted at 20.556 min (molecular weight 165 Dalton), it started to appear for O_3/H_2O_2 at the used-ozone dose of 3.6 g O_3/L leachate (Figure 3.20) and for O_3 only at the used-ozone dose of 3.7 g O_3/L leachate (Figure 3.21), and increased when the used-ozone dose increased from 3.7 to 9.2 g O_3/L leachate for O_3 only and from 5.1 to 10.3 g O_3/L leachate for O_3/H_2O_2 (Figures 3.17 and 3.18). This peak for O_3 only was

smaller than that for O_3/H_2O_2 at the used-ozone dose from 3.7 to 9.2 g O_3/L leachate for O_3 only and from 5.1 to 10.3 g O_3/L leachate for O_3/H_2O_2 (Figures 3.21 to 3.24). However, this peak was larger for O_3 only than that for O_3/H_2O_2 at the used-ozone dose of 12.5 g O_3/L leachate for O_3 only and 13.8 g O_3/L leachate for O_3/H_2O_2 (Figure 3.25). This might be explained as most of the large molecules being oxidized at the used-ozone dose of 12.5 g O_3/L leachate for O_3 only and 13.8 g O_3/L leachate for O_3/H_2O_2, and the organic compounds with molecular weight of 165 Dalton started to be oxidized in O_3/H_2O_2 process.

4) The new peak, shown as the toe berm on the left of the peak at 19.700 min (molecular weight of 287 Dalton), appeared in both O_3 only and O_3/H_2O_2 at the used-ozone dose of 3.7 g O_3/L leachate for O_3 only and 5.1 g O_3/L leachate for O_3/H_2O_2 (Figure 3.21), and increased with increased used-ozone dose from 3.7, to 12.8 g O_3/L leachate for O_3 only and from 5.1 to 13.8 g O_3/L leachate for O_3/H_2O_2 (Figures 3.17 and 3.18). There is no obvious difference between these peaks for O_3 only and O_3/H_2O_2 at the same applied-ozone dose.

One of the objectives of this research was to understand the oxidation process of O_3 only and O_3/H_2O_2 by taking advantage of the molecular size distribution analysis. A widely accepted viewpoint about the oxidation of old or biologically treated landfill leachate, especially for O_3 only, is that the large refractory molecules are broken down to small molecules, which are biodegradable (Langlais et al. 1991; 1989; Beltran-Heredia et al. 2000; Baig and Liechti, 2001; Geenens et al. 2001). Figure 3.12 shows the highest BOD_5 values occurred at the used-ozone dose of 2.6 g O_3/L leachate for O_3 only and 3.6 g O_3/L leachate for O_3/H_2O_2. However, the new peak with molecular weight of 165 Dalton only

appeared in O_3/H_2O_2 oxidation and was not observed in O_3 oxidation at the used-ozone dose of 2.6 g O_3/L leachate for O_3 only and 3.6 g O_3/L leachate for O_3/H_2O_2. The new peak as the toe berm on the left of the peak at 19.700 min (molecular weight 287 Dalton) also did not appear at these used-ozone doses (Figure 3.20). Therefore, there was no obvious correlation observed between the new peak formation and the BOD_5 increase. It is possible that the BOD_5 increase was caused by molecular structure changes due to the oxidation with O_3 only or O_3/H_2O_2.

3.4 Conclusions

Aged raw leachate (pH = 8.30 and treatment temperature = 22°C) was oxidized with O_3 only and O_3/H_2O_2 at different used-ozone doses. The following conclusions were drawn from the results of this research:

1. The addition of H_2O_2 to leachate right before ozonation marginally enhanced COD reduction at lower used-ozone doses. However, the difference between CODs after O_3 only and after O_3/H_2O_2 became less pronounced with the increase of used-ozone dose. At a 95% of confidence level, the difference between the CODs of O_3 only and of O_3/H_2O_2 was not statistically significant.
2. BOD_5 increased after oxidation with O_3 only or O_3/H_2O_2, and BOD_5 of both treatments had the same increase trends. BOD_5 after oxidation with O_3 only were always higher than those treated with O_3/H_2O_2 at the lower used-ozone doses. The highest BOD_5 value occurred at the used-ozone dose of 2.6 g O_3/L leachate for O_3 only and 3.6 g O_3/L leachate for O_3/H_2O_2.

3. Ratio of BOD_5/COD was 0.136 for O_3 only and 0.140 for O_3/H_2O_2, respectively, at the used-ozone dose of 2.6 g O_3/L leachate for O_3 only and 3.6 g O_3/L leachate for O_3/H_2O_2. Therefore, the aged raw leachate became biodegradable after oxidation with O_3 only or O_3/H_2O_2 at these used-ozone doses, and it can be recycled to the RBC unit. At a 95% of confidence level, the difference in the ratios of BOD_5/COD of O_3 only and of O_3/H_2O_2 was not statistically significant.
4. At the used-ozone dose of 1.2 g O_3/L leachate for O_3 only and 1.8 g O_3/L leachate for O_3/H_2O_2, colour removal efficiency was 90%.
5. NH_3-N and alkalinity decreased linearly with the used-ozone dose increase; while nitrite+nitrate increased linearly with the used-ozone dose increase. At a 95% of confidence level, the difference in the NH_3-Ns and in the alkalinities of O_3 only and of O_3/H_2O_2 was statistically insignificant.
6. The addition of H_2O_2 at the dose of 0.63 g H_2O_2/L leachate marginally enhanced the reduction of the peaks with molecular weight larger than 1,680 Dalton at lower used-ozone doses. The peaks with molecular weight larger than 1,680 Dalton became small with the used-ozone dose increase. However, the peak with molecular weight of 287 Dalton did not change very much when used-ozone dose increased. Meanwhile, the oxidation by-products shown as the peak at 20.556 min (molecular weight 165 Dalton) and the toe berm on the left of the peak at 19.700 min (molecular weight 287 Dalton) increased when the of the used-ozone dose increased. There is no obvious correlation observed between the new peak formation and the BOD_5 increase.

3.5 References

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CHAPTER 4 AGED RAW LANDFILL LEACHATE: MEMBRANE FRACTIONATION, O_3 ONLY AND O_3/H_2O_2 OXIDATION AND MOLECULAR SIZE DISTRIBUTION ANALYSIS [3]

4.1 Introduction

The major components of the aged landfill leachate are large refractory organic molecules such as humic substances, which include humic acids and fulvic acids (Chian 1977; Lecoupannec 1999) with molecular weight within 1,000 to 10,000 Dalton. This is due to the stabilization of most of its biodegradable fraction during the aging process.

Membrane fractionation has been applied to the characterization of raw landfill leachate (Park et al. 2001) and the landfill leachates after electron-beam radiation process (Bae et al. 1999) or after biological treatment process (Gourdon et al.1989; Yoon et al. 1998; Bae et al.1999; Park et al. 2001). Fractionation of landfill leachate with different molecular weight cut-off (MWCO) membranes can cause organic compounds of different molecular weights to end up in different samples. Therefore, oxidation of such fractionated samples would reveal the behaviours of the organic compounds of different molecular weights during the oxidation processes. Also, this would lead to more understanding of the characteristics of these compounds when they are subjected to the oxidation treatments. In the research by Yoon et al. (1998), the aerated lagoon effluents were fractionated with

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1,000 molecular weight cut-off (MWCO) and 500 MWCO membranes. Then, coagulation and Fenton reaction were applied to the fractionated samples, respectively. In that study, they only investigated the TOC removal efficiency. To date, very little or virtually no research has been done with regard to oxidation of fractionated landfill leachate with O_3 and O_3/H_2O_2.

Most of the molecular size distribution analyses were performed to characterize the molecular weights of organic compounds present in raw landfill leachates (Chian 1977; Lecoupannec 1999). Imai et al. (1998) analyzed the molecular size distribution change of landfill leachate before and after ozonation with high performance liquid chromatograph (HPLC) equipped with gel filtration column and UV detector, with an eluant of 0.3 M NaCl in 0.1 M pH = 7 phosphate buffer at a flow rate of 0.8 mL/min. There is no information available regarding the molecular size distribution change of the fractionated landfill leachates before and after oxidation with O_3 only or O_3/H_2O_2.

The complexation of cadmium (Cd) by organic components of the landfill leachates has been known for more than twenty years (Knox and Jones 1979). This complexation was attributed to the organic compounds with phenolic hydroxyl groups (Knox and Jones 1979; Livens 1991) having stability constant towards Cd of the order of 105. Lun and Christensen (1989) further confirmed the complexation of organic compounds in leachates with the Cd ions by spiking Cd solution into five Danish municipal landfill leachates, and then determined free divalent Cd and complexed Cd. Christensen et al. (1996) found the ability of dissolved organic carbon from landfill leachate polluted groundwater to form complexes with the heavy metals Cd, nickel (Ni) and zinc (Zn) was in the order Zn<Cd<Ni. Jensen and Christensen (1999) investigated the distributions of metals in the

colloidal fractions and dissolved fractions of four Danish landfill leachates. From their research, calcium (Ca) and manganese (Mn) were about equally distributed between the dissolved fractions and the colloidal fractions, whereas iron (Fe) was found mostly in the colloidal fractions; 10-60% of the total content of Ni, 0-95% of the total content of Zn, and 30 to 100% of the total content of copper (Cu) were associated with the colloidal fractions; Cd was found primarily in the truly dissolved fraction (26-100%); and lead (Pb) and chromium (Cr) that distributed between colloidal and dissolved species varied among the leachate samples. Jensen et al. (1999) found that dissolved Cd, Cu, and Pb were mainly associated with dissolved organic carbon, while Ni was also present as carbonate complexes and Zn as carbonate complexes and free divalent Zn. Moreover, Jensen et al. (1999) found that very little metal was found in colloids larger than 0.40 μm. It has been reported that the fulvic acids could complex with Ca (Ephraim and Allard 1994a), Cd (Ephraim and Xu 1989), Cu (Ephraim and Allard 1994b), Fe (Ephraim 1992a), Strontium (Sr) and europium (Eu) (Norden et al. 1993) and Zn (Ephraim 1992b).

In this research, the fractionated samples as well as the aged raw leachate were oxidized with O_3 only and O_3/H_2O_2. COD, BOD_5 and colour of each sample before and after oxidation were measured. Also, the mass distribution profiles of COD, BOD_5, colour and metals of the aged raw leachate were developed through mass balance analysis between the aged raw leachate and the fractionated leachate samples. Meanwhile, the molecular size distribution of each sample before and after oxidation was also obtained with HPLC equipped with gel filtration column and UV detector at 254 nm. These data can reveal the behaviours of the organic compounds in the aged raw leachate with molecular

size of 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton; and <1,000 Dalton during the oxidation processes.

4.2 Materials and methods

4.2.1 Landfill leachate

The aged raw leachate was collected from the equalization storage tank of the Clover Bar Landfill Leachate Treatment Plant, Edmonton, Alberta, Canada. This landfill leachate had been stabilized in the equalization storage tank for about one year due to the pipeline modification for the five-stage biological rotating contactors (RBCs). Table 4.1 depicts the volume and average quality parameters of the aged raw leachate before fractionation.

Table 4.1 Volumes and average quality parameters of the aged raw leachate and the fractionated aged raw leachates.

Sample	Aged raw leachate	0.45 μm to 10,000 Dalton	10,000 to 5,000 Dalton	5,000 to 1,000 Dalton	<1,000 Dalton
Volume, mL	5,000	1,000	1,490	1,528	1,945
COD, mg/L	1,000 ± 0	429 ± 5	1,190 ± 5	850 ± 5	640 ± 5
BOD_5, mg/L	24 ± 2	4 ± 4	23 ± 3	24 ± 0	23 ± 2
Colour, TCU	1,090 ± 13	1,110 ± 7	1,360 ± 13	1,260 ± 13	107 ± 5
NH_3-N, mg N/L	451 ± 3	117 ± 4	424 ± 1	408 ± 4	408 ± 0
Alkalinity, mg/L as $CaCO_3$	4,010 ± 36	1,040 ± 36	3,880 ± 29	3,730 ± 36	3,630 ± 18
pH	8.41 ± 0.01	8.45 ± 0.01	8.52 ± 0.01	8.55 ± 0.01	8.29 ± 0.01

4.2.2 Experimental procedure and analysis methods

Figure 4.1 shows the membrane fractionation apparatus. The process for membrane fractionation is illustrated in Figure 4.2. Five thousand (5,000) mL aged raw leachate was filtered with 0.8 μm and 0.45 μm pore size filters, sequentially. 32 mL and 18 mL were lost in the 0.8 μm and 0.45 μm pore size filters, and 4,950 mL filtrate was obtained. This filtrate was further fractionated with 10,000 MWCO regenerated cellulose membrane (PLGC, 10k, Millipore Corporation, Bedford, MA, catalogue #: CDUF001LG) at 124.2 kPa. After the fractionation, the pressure of membrane cell was reduced to zero, the inlet tubing and retentate tubing were taken out of the feed flask and put into a beaker containing 200 mL ultra pure water (conductivity^{-1} > 18 MΩ). This ultra pure water was run for 2 min to wash out the organic compounds retained in membrane cell. Then, the pressure was increased to 124.2 kPa, and the filtrate was also collected into the filtrate flask during this washing period. The retentate in the beaker was poured into the retentate flask, and the volumes of retentate and filtrate were measured with graduated cylinders. Then, the retentate was diluted to 1,000 mL with volumetric flask and formed the sample of 0.45 μm to 10,000 Dalton to supply enough samples for the oxidation with O_3 and O_3/H_2O_2.

The process for the fractionation with 5,000 MWCO regenerated cellulose membrane (PLCC, 5k, Millipore Corporation, Bedford, MA, catalogue #: CDUF001LC) and 1,000 MWCO regenerated cellulose membrane (PLAC, 1k, Millipore Corporation, Bedford, MA, catalogue #: CDUF001LA) was the same as that of 10,000 MWCO membrane except that the retentate was not diluted. The volume and quality parameters of the four fractionated samples after membrane fractionation are also shown in Table 4.1.

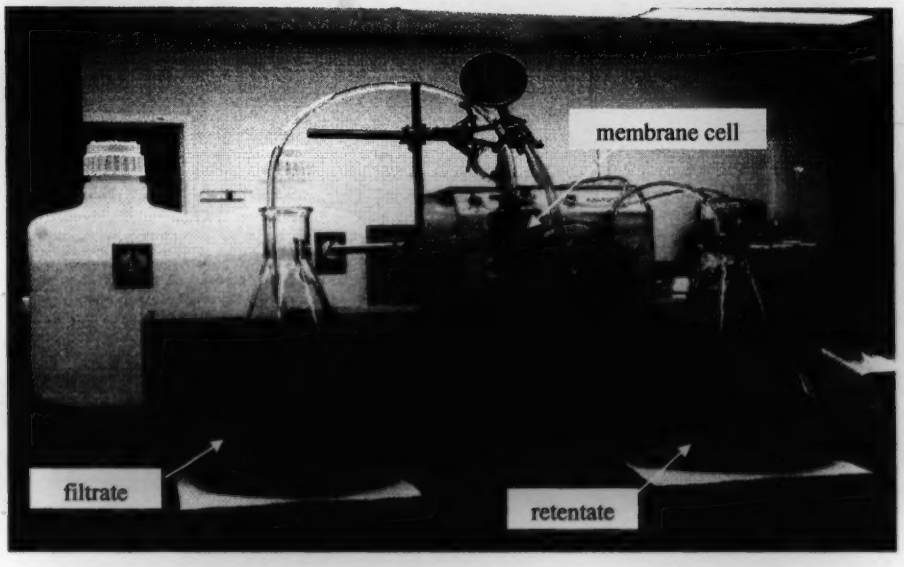

Figure 4.1 Apparatus for membrane fractionation.

The set-up and the procedure for sample oxidation with O_3 and O_3/H_2O_2 was the same as those described in section 3.2.2, Chapter 3. Ninety (90) L of ozonated oxygen gas (ozone concentration = 42 mg O_3/L) were applied to each sample. The leachate volume for each treatment was 250 mL. Therefore, the applied-ozone dose was 15.1 g O_3/L leachate. The dose of H_2O_2 was 1.26 g H_2O_2/L leachate for the sample of 10,000 to 5,000 Dalton, and 0.63 g H_2O_2/L leachate for the other samples.

COD, BOD_5, colour were determined following the Standard Methods (American Public Health Association et al. 1998). COD was analyzed in triplicate, and BOD_5 and colour were measured in duplicate. Method for molecular size distribution analysis was the same as that described in Sections 3.2.4.2 and 3.2.4.3, Chapter 3. The metals in the samples were analyzed by using ICP/MS at the Enviro-Test Laboratories, Edmonton, Alberta, Canada. The analytical methods for dissolved mercury (Hg) and dissolved low-

level trace metals were based on USEPA 6020, analytical method for dissolved major metals was based on USEPA 200.7.

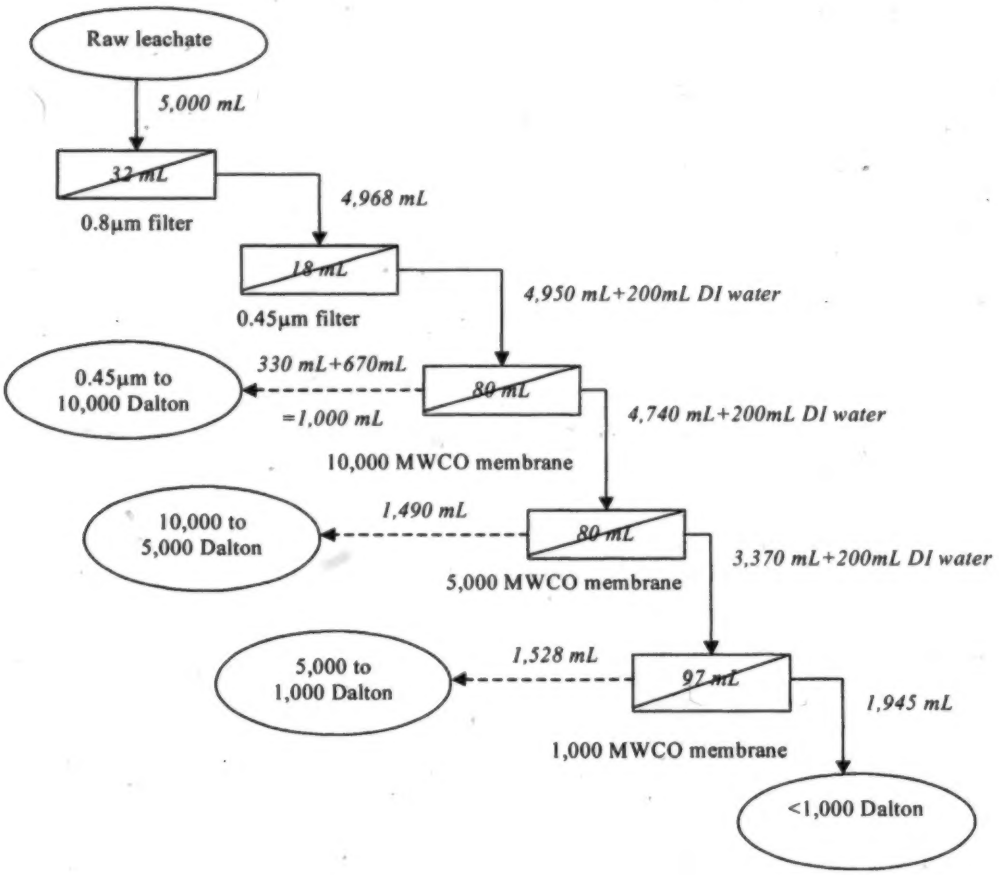

Figure 4.2 Schematic diagram of the membrane fractionation process.

4. 3 Results and discussion

4.3.1 Mass distribution profiles for COD, BOD_5, colour and metals

Figure 4.3 represents the mass distribution profiles for COD, BOD_5 and colour. These distribution profiles were obtained through mass balance analysis for COD, BOD_5

and colour of raw leachate, 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton; and <1,000 Dalton measured before oxidation. The organic compounds with molecular weight less than 10,000 Dalton were the major contributors of COD and BOD_5. The organic compounds with molecular weight larger than 1,000 Dalton were the major colour contributors.

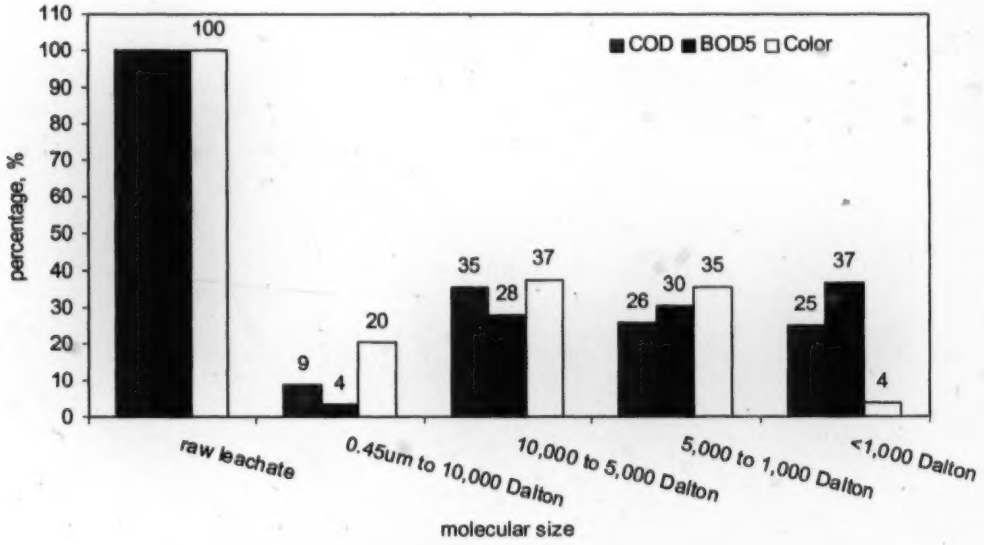

Figure 4.3 Mass distribution profiles of COD, BOD_5 and colour.

If the percentage for COD, BOD_5 or colour are added up, respectively, the sum of the percentages for each parameter was not exactly 100%. This might be due to a very small amount of organic compounds being lost either in the process of membrane separation or in the colloidal particles, which were removed by the 0.45 μm filter.

Table 4.2 depicts the metal mass distributions among each fractionated sample.

Table 4.2 Metal mass distribution of the aged raw leachate (mg) with measured recovery ratios.

Metal	Aged raw leachate	0.45 μm to 10,000 Dalton	10,000 to 5,000 Dalton	5,000 to 1,000 Dalton	<1,000 Dalton	Recovery ratio
Silver (Ag)	0.0035	0.0011 (31)	0.00045 (13)	0.0006 (20)	0.0004 (11)	75%
Aluminum (Al)	0.9	0.30 (33)	0.27 (30)	0.23 (26)	0.25 (28)	117%
Arsenic (As)	0.0045	0.0065 (144)	0.0046 (100)	0.0032 (71)	0.0023 (51)	366%
Boron (B)	107	7.97 (7)	33.4 (31)	29.2 (27)	38.1 (36)	101%
Barium (Ba)	0.61	0.0491 (8)	0.209 (34)	0.177 (29)	0.243 (40)	111%
Bismuth (Bi)	0.00125	0.00006 (5)	0.00019 (15)	0.00023 (18)	0.00037 (30)	68%
Calcium (Ca)	66.0	5.5 (8)	20.0 (30)	18.8 (28)	25.1 (38)	104%
Cadmium (Cd)	0.0205	0.0053 (26)	0.0088 (43)	0.0079 (39)	0.0089 (43)	151%
Cobalt (Co)	0.0935	0.0097 (10)	0.0539 (58)	0.0200 (21)	0.0068 (7)	96%
Chromium (Cr)	0.152	0.0612 (40)	0.1317 (87)	0.0191 (13)	<0.0008 (0.5)	140.5%
Copper (Cu)	0.079	0.0137 (17)	0.0523 (66)	0.0402 (51)	0.0445 (56)	190%
Iron (Fe)	4.285	1.36 (32)	2.04 (48)	0.402 (9)	0.239 (6)	95%
Mercury (Hg)	0.0055	0.0031 (56)	0.0022 (40)	0.0009 (16)	0.00156 (28)	140%
Potassium (K)	***2,295***	***122 (5)***	***662 (29)***	***641 (28)***	***875 (38)***	***100%***
Magnesium (Mg)	1,525	87.9 (6)	468 (31)	445 (29)	550 (24)	90%
Manganese (Mn)	0.075	<0.01 (13)	0.018 (24)	0.023 (31)	0.021 (28)	96%
Molybdenum (Mo)	0.019	0.0041 (22)	0.0060 (32)	0.0043 (23)	0.0049 (26)	103%
Sodium (Na)	***8,350***	***458 (5)***	***2,399 (29)***	***2,323 (28)***	***3,209 (38)***	***100%***
Nickel (Ni)	1.455	0.109 (7)	0.614 (42)	0.377 (26)	0.323 (22)	97%
Lead (Pb)	0.006	0.0011 (18)	0.0045 (75)	0.0041 (68)	0.0045 (75)	236%
Antimony (Sb)	0.021	0.0018 (9)	0.0082 (39)	0.0049 (23)	0.0047 (22)	93%
Selenium (Se)	0.2115	0.0112 (5)	0.0600 (28)	0.0527 (25)	0.0737 (35)	93%
Tin (Sn)	0.0265	0.0077 (29)	0.0125 (47)	0.0035 (13)	0.0031 (12)	101%
Strontium (Sr)	3.855	0.236 (6)	1.177 (30)	0.984 (26)	1.344 (35)	97%
Titanium (Ti)	0.0975	0.0250 (26)	0.0355 (36)	0.0147 (15)	0.0177 (18)	95%
Vanadium (V)	0.160	0.0094 (6)	0.0224 (14)	0.134 (84)	0.080 (5)	109%
Zinc (Zn)	0.075	0.014 (19)	0.049 (65)	0.046 (60)	0.041 (55)	199%

Note: The numbers in the brackets were the metal mass percentage; the recovery ratio was obtained by adding up the mass percentage of every species in each fractionated sample.

Table 4.3 Metal mass distribution of the aged raw leachate (mg) with normalized recovery ratios.

Metal	Aged raw leachate	0.45 μm to 10,000 Dalton	10,000 to 5,000 Dalton	5,000 to 1,000 Dalton	<1,000 Dalton	Recovery ratio
Silver (Ag)	0.0035	0.0011 (41)	0.00045 (17)	0.0006 (27)	0.0004 (15)	100%
Aluminum (Al)	0.9	0.30 (28)	0.27 (26)	0.23 (22)	0.25 (24)	100%
Arsenic (As)	0.0045	0.0065 (39)	0.0046 (27)	0.0032 (19)	0.0023 (14)	100%
Bismuth (Bi)	0.00125	0.00006 (7)	0.00019 (22)	0.00023 (26)	0.00037 (44)	100%
Cadmium (Cd)	0.0205	0.0053 (17)	0.0088 (28)	0.0079 (26)	0.0089 (28)	100%
Chromium (Cr)	0.152	0.0612 (28)	0.1317 (62)	0.0191 (9)	<0.0008 (0.4)	100%
Copper (Cu)	0.079	0.0137 (9)	0.0523 (35)	0.0402 (27)	0.0445 (29)	100%
Mercury (Hg)	0.0055	0.0031 (40)	0.0022 (29)	0.0009 (11)	0.00156 (20)	100%
Potassium (K)	***2,295***	***122 (5)***	***662 (29)***	***641 (28)***	***875 (38)***	***100%***
Sodium (Na)	***8,350***	***458 (5)***	***2,399 (29)***	***2,323 (28)***	***3,209 (38)***	***100%***
Lead (Pb)	0.006	0.0011 (8)	0.0045 (32)	0.0041 (29)	0.0045 (32)	100%
Zinc (Zn)	0.075	0.014 (10)	0.049 (33)	0.046 (30)	0.041 (28)	100%

Note: The numbers in the brackets were obtained by dividing the mass percentage in the brackets in Table 4.2 with its recovery ratio in Table 4.2 for every species.

It is for sure that the potassium (K) and sodium (Na) were totally dissolved in water, therefore, the recovery ratios for both species were 100%. Coincidentally, the percentages of K and Na among the fractionated samples were in agreement with the BOD_5 mass distribution. This might suggest that the BOD_5-causing organic compounds existed in the leachate freely and totally dissolved in water.

The recovery ratios of B, Ca, Co, Fe, K, Mn, Mo, Na, Ni, Sn, Sr, and Ti were within (100 ± 5)%. The recovery ratios of Ba, Mg, Sb, Se, and V were within (100 ± 10)%. The percentages of K and Na in 0.45 μm to 10,000 Dalton, 10,000 to 5,000 Dalton, 5,000 to 1,000 Dalton and <1,000 Dalton were 5%, 29%, 28% and 38%, respectively. The

percentages of K and Na were set up as references, the percentages of other species with recovery ratio in the range of (100 ± 10)% were compared to the references, it was found that Co, Fe, Ni, Sb, Sn and Ti were enriched in the samples of 0.45 μm to 10,000 Dalton and 10,000 to 5,000 Dalton; and V was enriched in the sample of 5,000 to 1,000 Dalton.

For the metal species with recovery ratio beyond the range of (100 ± 10)%, their normalized recovery ratios are shown in Table 4.3. Ag, Al, As, Cd, Cr, Cu, Hg, Pb and Zn tended to accumulate in the sample of 0.45 μm to 10,000 Dalton; Cr, Cu, Pb and Zn were also enriched in the sample of 10,000 to 5,000 Dalton; and Bi was enriched in the sample of <1,000 Dalton.

4.3.2 Used-ozone dose

Figure 4.4 shows the used-ozone dose for O_3 only and O_3/H_2O_2 at the applied-ozone dose of 15.1 g O_3/L leachate.

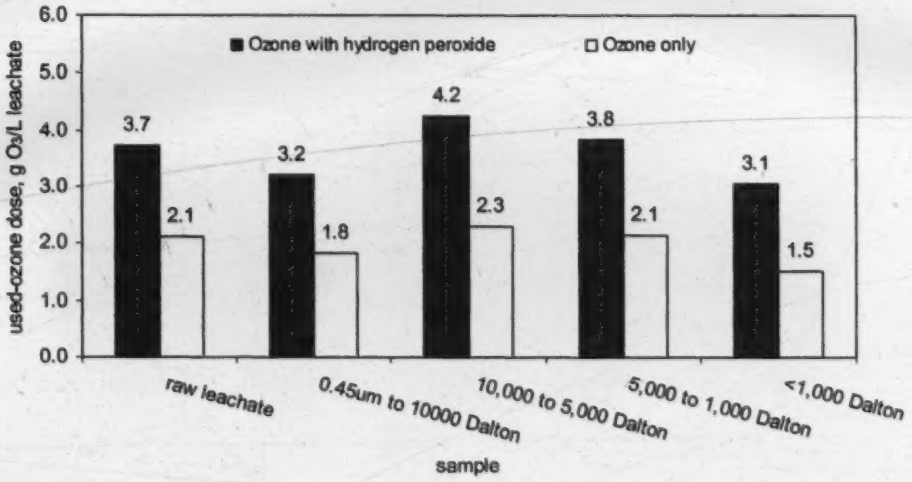

Figure 4.4 Used-ozone dose for O_3 only and O_3/H_2O_2 at applied-ozone dose of 15.1 g O_3/L leachate.

The used-ozone dose for each sample was not the same although every sample was oxidized at the equal applied-ozone dose. Such results may suggest that the potential of each sample to react with ozone was different due to the different amount of the organic compounds in each sample. Moreover, the addition of H_2O_2 increased the ozone utilization ratio because H_2O_2 was the initiator of ozone decomposition.

4.3.3 Chemical oxygen demand (COD)

Figure 4.5 depicts the COD of each sample before and after oxidation with O_3 only and O_3/H_2O_2. The addition of H_2O_2 marginally enhanced the reduction of COD for all of the samples.

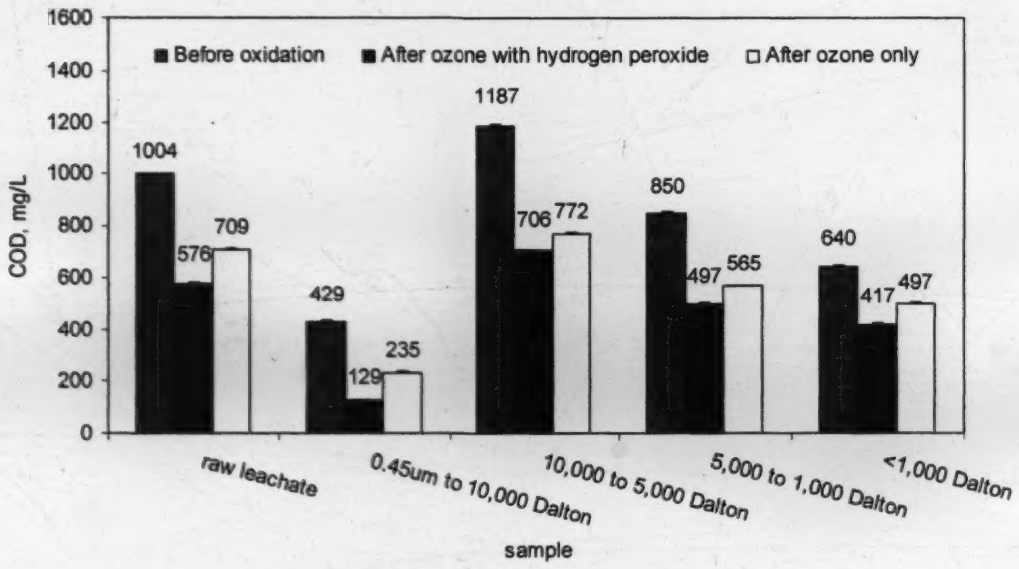

Figure 4.5 COD before and after oxidation with O_3 only and O_3/H_2O_2.

The difference between CODs after O_3 only and after O_3/H_2O_2 treatment was 133, 106, 66, 68, and 80 mg/L for raw leachate; 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton and <1,000 Dalton, respectively. These results indicated that

the addition of H_2O_2 was less effective in COD reduction for samples of 10,000 to 5,000 Dalton and 5,000 to 1,000 Dalton even though the H_2O_2 dose was 1.26 g H_2O_2/L leachate for 10,000 to 5,000 Dalton and 0.63 g H_2O_2/L leachate for 5,000 to 1,000 Dalton. Therefore, the COD caused by the organic compounds with molecular weight from 10,000 to 1,000 Dalton was less susceptible to the oxidation with either O_3 only or O_3/H_2O_2. For these organics, the small COD difference between O_3 only and O_3/H_2O_2 may also be because these organics having more carbon-to-carbon double bonds, nitrogen-to-nitrogen double bonds or benzene rings, which were vulnerable to the attack of molecular ozone; therefore, the combination of O_3 with H_2O_2 had little advantage over O_3 only on the COD reduction for these two samples.

4.3.4 Five-day biochemical oxygen demand (BOD_5)

Figure 4.6 shows the BOD_5 values before and after oxidation with O_3 only and O_3/H_2O_2.

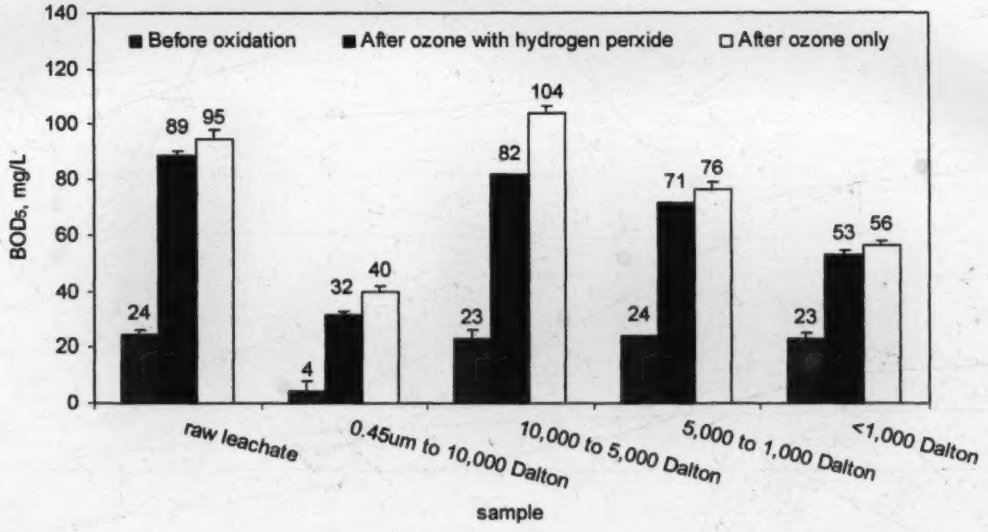

Figure 4.6 BOD_5 before and after oxidation with O_3 only and O_3/H_2O_2.

After oxidation, BOD_5 increased for each sample, and the BOD_5 increased more after oxidation with O_3 only than with O_3/H_2O_2. For O_3 only, the increased BOD_5 after oxidation was 71, 36, 81, 52, and 33 mg/L for the aged raw leachate, 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton; and <1,000 Dalton samples, respectively. For O_3/H_2O_2, the increased BOD_5 after oxidation is 65, 28, 69, 47, and 30 mg/L for the aged raw leachate, 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton; and <1,000 Dalton samples, respectively. More BOD_5 increase occurred for the fractions of 10,000 to 5,000 Dalton and 5,000 to 1,000 Dalton, which indicated that these two fractions became more biodegradable after oxidation with O_3 only or O_3/H_2O_2. These results might also suggest that the organic compounds with molecular weight from 10,000 to 1,000 Dalton contain more carbon-to-carbon double bonds, nitrogen-to-nitrogen double bonds or benzene rings. Once these structures were cleaved, the formation of cleaved organic compounds might lead to higher BOD_5.

The difference between BOD_5 after oxidation with O_3 only and O_3/H_2O_2 was 6, 8, 22, 5, and 3 mg/L for the aged raw leachate, 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton; and <1,000 Dalton samples, respectively. The largest standard deviation of BOD_5 tested in this research was 4.0 mg/L. Therefore, the difference, between BOD_5 after oxidation with O_3 only and O_3/H_2O_2 for the samples of the aged raw leachate, 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton, was significant. The difference between BOD_5 after oxidation with O_3 only and O_3/H_2O_2 for the sample of 10,000 to 5,000 Dalton might have been caused by the higher H_2O_2 dose. The higher the H_2O_2 dose, the more •OH radicals might have been formed, and the more

organic compounds might have been completely oxidized, thus leading to a lower BOD_5 after oxidation with O_3/H_2O_2.

4.3.5 Ratio of BOD_5/COD

Figure 4.7 shows the ratios of BOD_5/COD before and after oxidations with O_3 only and O_3/H_2O_2. The ratio of BOD_5/COD after O_3/H_2O_2 was higher than that after O_3 only for the aged raw leachate, 0.45 μm to 10,000 Dalton; 5,000 to 1,000 Dalton; and <1,000 Dalton samples. However, the ratio of BOD_5/COD after O_3/H_2O_2 was lower than that after O_3 only for the sample of 10,000 to 5,000 Dalton because higher H_2O_2 dose (1.26 g H_2O_2/L leachate) was added to this sample and possibly more •OH radicals were formed. The •OH radicals might have caused complete oxidation of organic compounds and resulted in less BOD_5 and lower ratio of BOD_5/COD. Therefore, if the objective of oxidation is to improve the ratio of BOD_5/COD; i.e., increase biodegradability, H_2O_2 dose of 0.63 g H_2O_2/L leachate will give higher ratio of BOD_5/COD than 1.26 g H_2O_2/L leachate for O_3/H_2O_2.

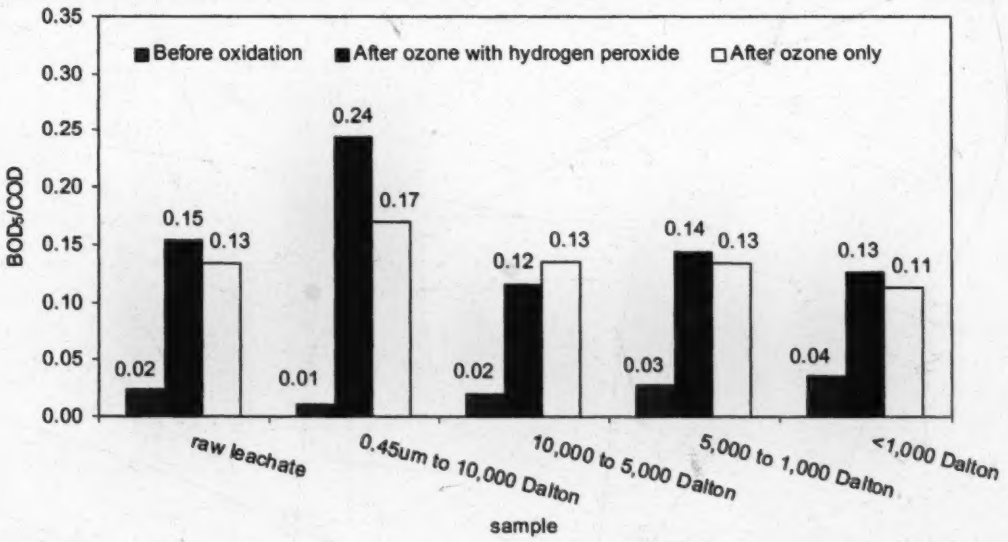

Figure 4.7 BOD_5/COD before and after oxidations with O_3 only and O_3/H_2O_2.

4.3.6 Colour

Figure 4.8 shows the colour of each sample before and after oxidation with O_3 only and O_3/H_2O_2. Colour removal efficiencies of the aged raw leachate, 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; and 5,000 to 1,000 Dalton samples were all above 87%, but colour removal efficiency of the sample of <1,000 Dalton was 69% for O_3/H_2O_2 and 51% for O_3 only.

The colour of the samples of 10,000 to 5,000 Dalton after oxidation were the highest among the five samples, which may imply that this sample had more colour causing compounds that could not be easily oxidized.

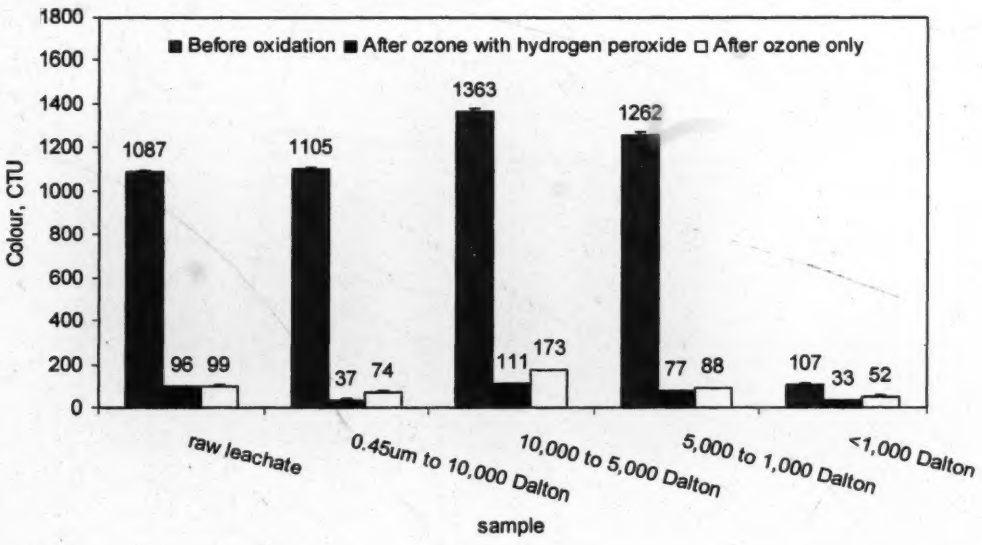

Figure 4.8 Colour before and after oxidation with O_3 only and O_3/H_2O_2.

4.3.7 Ratio of COD removed to used-ozone dose

Figure 4.9 shows the ratio of COD removed (CODr) to the used-ozone dose for

both treatments. The difference between the ratios of CODr/used-ozone dose of O_3 only and O_3/H_2O_2 were 24, 12, 57, 42, and 21 mg COD/g O_3 for the aged raw leachate, 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton and <1,000 Dalton, respectively. The highest difference of the ratio of CODr/used-ozone dose occurred in the sample of 10,000 to 5,000 Dalton. This might be attributed to two reasons. First, it was because this sample likely had more double bonds or aromatic structures, and these structures were easily broken down by molecular ozone. Consequently, more COD was removed by O_3 only. Second, higher H_2O_2 dose (1.26 g H_2O_2/L leachate for this sample, and 0.63 g H_2O_2/L leachate for other samples) was applied to this sample, and H_2O_2 was the initiator of ozone decomposition, thus causing a high used-ozone dose and a lower ratio of CODr/used-ozone dose.

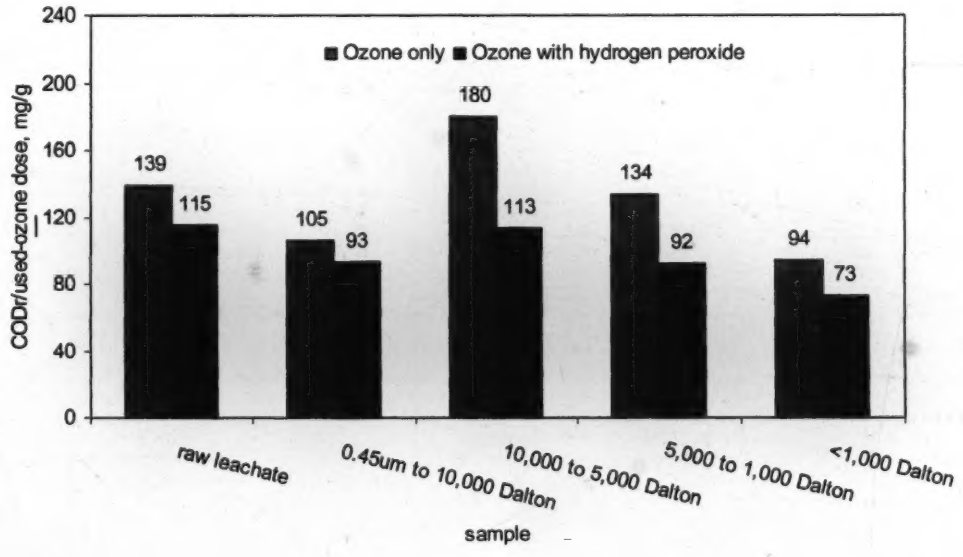

Figure 4.9 Ratio of COD removed to used-ozone dose for O_3 only and O_3/H_2O_2.

The second largest difference of CODr/used-ozone dose between both treatments happened to the sample of 5,000 to 1,000 Dalton. Since the H_2O_2 dose was 0.63 g H_2O_2/L leachate, the high ratio of CODr/used-ozone dose would likely be attributed to the molecular structures of this sample. As the same with the sample of 10,000 to 5,000 Dalton, this sample also likely had more double bonds and aromatic structures, therefore, more COD was removed by O_3 only at lower used-ozone dose, resulting in a large difference of CODr/used-ozone dose for both treatments.

4.3.8 Molecular size distribution

Figures 4.10 to 4.14 depict the molecular size distributions of the aged raw leachate, 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton; and <1,000 Dalton samples before and after oxidation with O_3 only and with O_3/H_2O_2. The molecular weight of each peak was determined based on its elution time and the standard curve of the molecular size distribution of the column G3000PW$_{XL}$ as shown in Figure 3.10, Chapter 3. This analysis was summarized in Table 4.4.

Table 4.4 Molecular weight (MW, Dalton) versus elution time (*t*, min).

Sample	Peak 1#		Peak 2#		Peak 3#		Peak 4#		Peak 5#	
	t	MW	*t*	MW	*t*	MW	*t*	MW	*t*	MW
Aged raw leachate	14.805	6,840	15.531	4,270	16.974	1,680	19.700	287	20.556	165
0.45 μm to 10,000 Dalton	14.325	9,330	14.733	7,160	15.436	4,540	16.856	1,810	19.145	411
10,000 to 5,000 Dalton	14.789	6,900	15.475	4,430	16.600	2,140	19.636	299	20.425	179
5,000 to 1,000 Dalton	14.811	6,810	15.506	4,340	16.939	1,720	19.625	301	20.500	171
<1,000 Dalton	14.831	6,720	15.503	4,350	16.953	1,700	19.625	301	20.408	181

Table 4.4 shows that there is inconsistencies between the molecular weight estimated with HPLC and gel filtration column and the molecular weight determined with

MWCO membranes. Specifically, the molecular weights of all the peaks in the sample of 0.45 μm to 10,000 Dalton were less than 10,000 Dalton (Figure 4.11). Also, the molecular weight of the first peak in the sample of 5,000 to 1,000 Dalton was 6,810 Dalton (Figure 4.13); and the molecular weights of the first three peaks in the sample of <1,000 Dalton were 6,720 Dalton, 4,350 Dalton and 1,700 Dalton (Figure 4.14). These inconsistencies might have been due to the following reasons:

1) The shape of the molecule. If a molecule has a slender shape, it is able to pass through the pore of the membrane; therefore, it can end up in the filtrate even though its molecular weight is larger than that of the membrane can cut off. On other hand, if a molecule has a spherical shape, it will have a larger diameter. Thus it is not able to pass through the pore of the membrane, and remains in the retentate even though its molecular weight is smaller than that of the membrane can cut off.

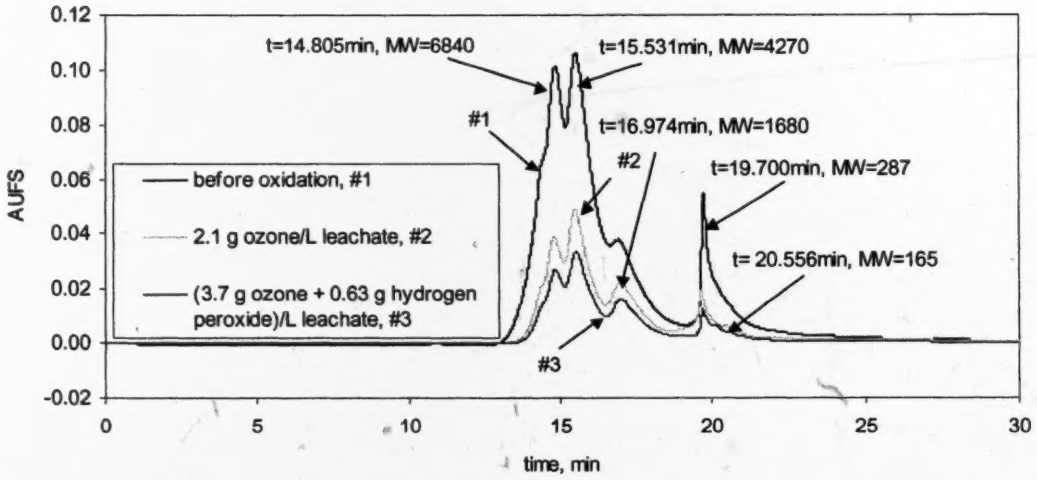

Figure 4.10 Molecular size distributions of aged raw leachate before and after oxidation (initial pH = 8.41, treatment temperature = 22°C).

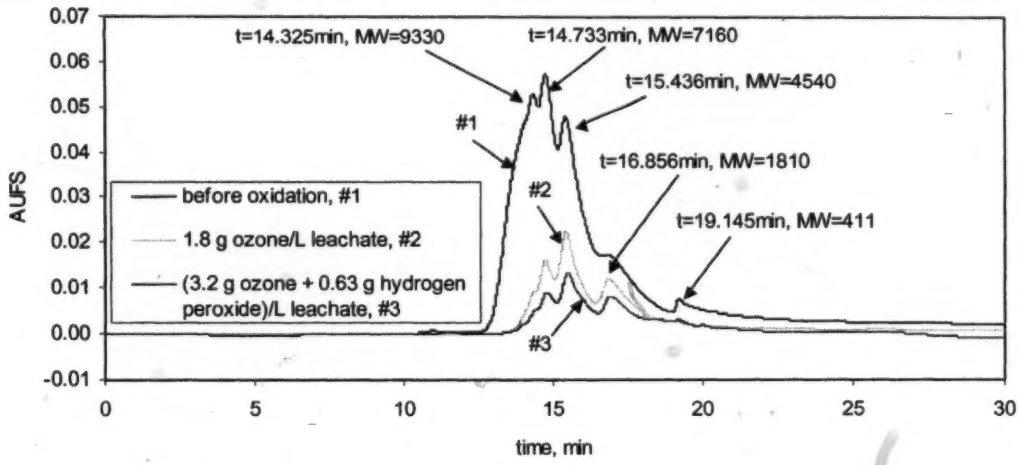

Figure 4.11 Molecular size distributions of 0.45 μm to 10,000 Dalton before and after oxidation (initial pH = 8.45, treatment temperature = 22°C).

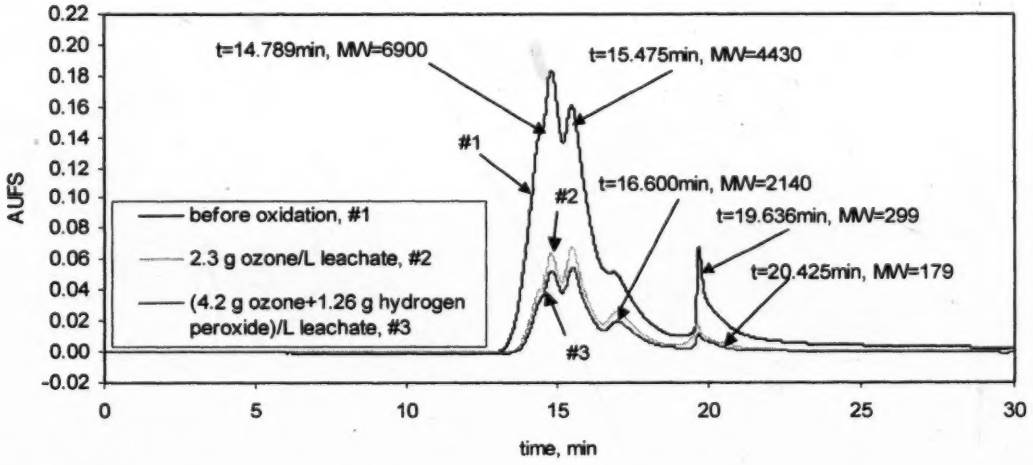

Figure 4.12 Molecular size distributions of 10,000 to 5,000 Dalton before and after oxidation (initial pH = 8.52, treatment temperature = 22°C).

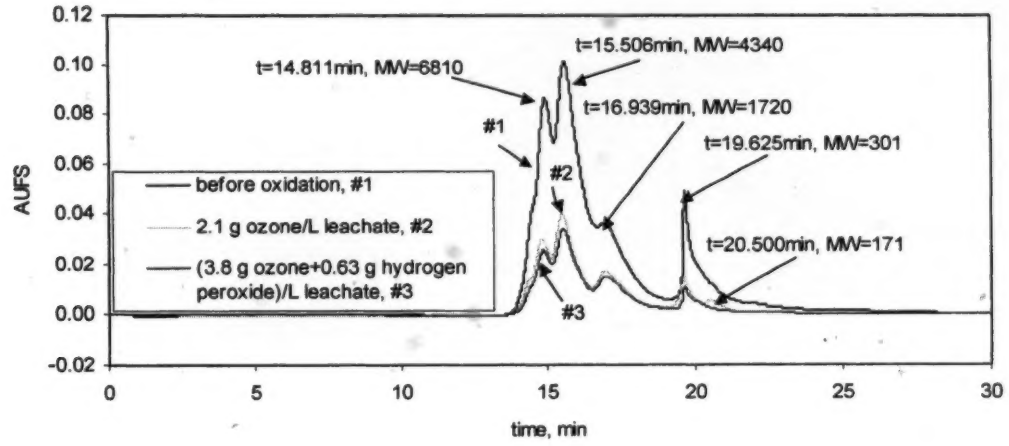

Figure 4.13 Molecular size distributions of 5,000 to 1,000 Dalton before and after oxidation (initial pH = 8.55, treatment temperature = 22°C).

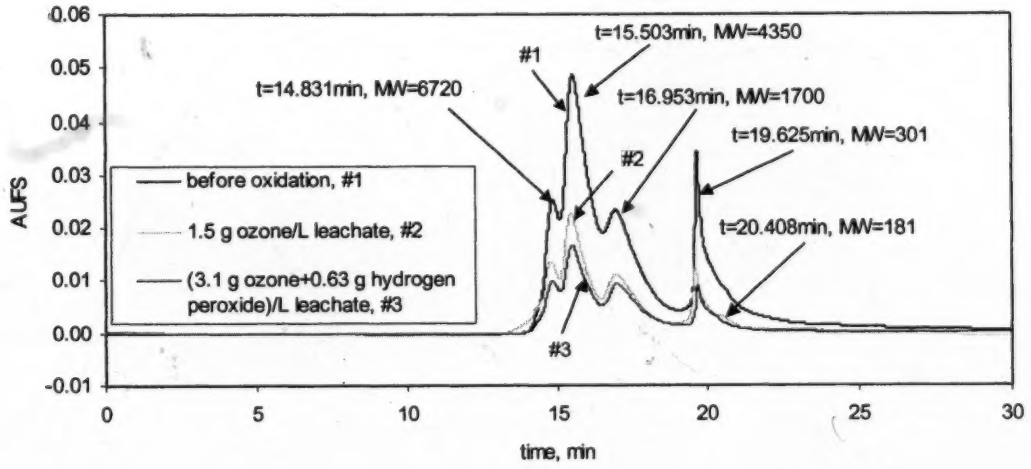

Figure 4.14 Molecular size distributions of <1,000 Dalton before and after oxidation (initial pH = 8.29, treatment temperature = 22°C).

2) The compression of the molecule. If a molecule has a loose structure, it is easier to be compressed under the pressure of 124.2 kPa. Therefore, it is able to pass through the pore of the membrane, and can end up in the filtrate even though its molecular weight is larger than the molecular weight that the membrane can cut off, and vice versa.

Ideally, the fraction of a specific molecular size range should only contain the compounds with the same molecular weight range. In fact, each fraction also contains some small molecules. For example, compounds with molecular weight less than 1,000 Dalton also showed up in the samples 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; and 5,000 to 1,000 Dalton (Figures 4.11 to 4.13). This phenomenon was due to the process of membrane separation since it was impossible for each fraction with large molecular weight compounds to be filtered until a "dry" condition was reached. Therefore, it still contained some amount of small molecules.

Although the membrane process has the shortcomings mentioned above, it can fractionate the organic compounds and metals in the aged raw leachate, which has been proved by the distributions of COD, BOD_5, colour and metals.

As far as the samples after oxidation are considered, the addition of H_2O_2 enhanced the reduction of the peaks with molecular weights larger than 1,000 Dalton. The effect of H_2O_2 addition was most obvious for the samples of aged raw leachate (Figure 4.10); 0.45 μm to 10,000 Dalton (Figure 4.11); and <1,000 Dalton (Figure 4.14); but likely insignificant for the samples of 10,000 to 5,000 Dalton (Figure 4.12) and 5,000 to 1,000 Dalton (Figure 4.13). These results may be explained as follows: the fraction of 10,000 to 1,000 Dalton of the aged raw leachate might have had more carbon-to-carbon double

bonds, nitrogen-to-nitrogen double bonds and/or aromatic structures, which were sensitive to the molecular ozone attack. Therefore, O_3/H_2O_2 oxidation did not show a large advantage over O_3 only oxidation. The results of molecular size distributions after oxidation were also consistent with the result of COD after oxidation.

There were no new peaks observed in any of the samples after oxidation with O_3/H_2O_2. After oxidation with O_3 only, no new peaks were observed for the 0.45 μm to 10,000 Dalton sample (Figure 4.11); new peaks were observed with molecular weights of 165, 179, 171, and 181 Dalton, respectively, in the samples of aged raw leachate, 10,000 to 5,000 Dalton, 5,000 to 1,000 Dalton, and <10,000 Dalton.

After oxidation with O_3 only, BOD_5 increased (Figure 4.6). Figure 4.15 depicts the molecular size distribution of these five samples after oxidation with O_3 only. The higher the BOD_5 of the sample, the larger the total peak area of molecular size distribution of that sample. The BOD_5 of each sample after oxidation with O_3 only was plotted against its total peak area (Figure 4.16).

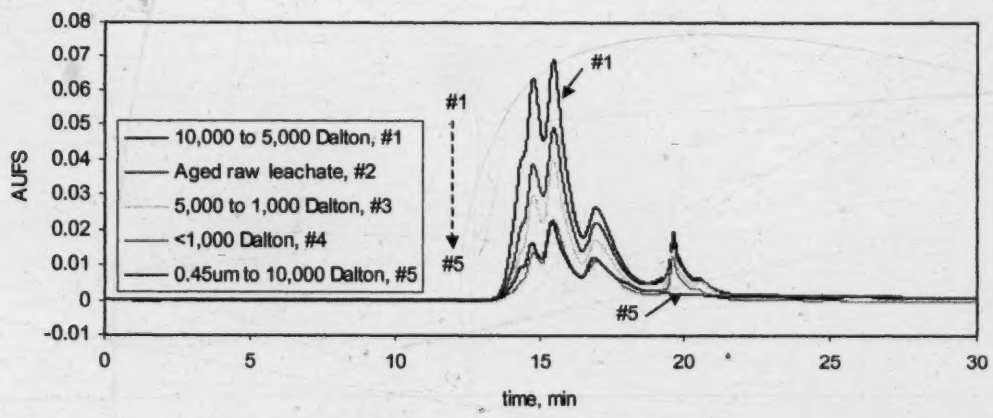

Figure 4.15 Molecular size distribution of each sample after oxidation with O_3 only.

Figure 4.16 indicates that BOD_5 of each sample after oxidation with O_3 only could be represented as a logarithmic function of its total peak area. On the other hand, the peak area of the new peak after O_3 only of 10,000 to 5,000 Dalton; aged raw leachate; 5,000 to 1,000 Dalton; <1,000 Dalton; and 0.45 μm to 10,000 Dalton accounts for 3.7%; 4.5%; 5.4%; 5.6%; and 0% of its total peak area, respectively. Therefore, there was no correlation observed between the BOD_5 after oxidation and the peak areas of the new peaks formed after oxidation. On the contrary, the BOD_5 after oxidation with O_3 only were correlated with the amount of large molecular organic compounds in the sample.

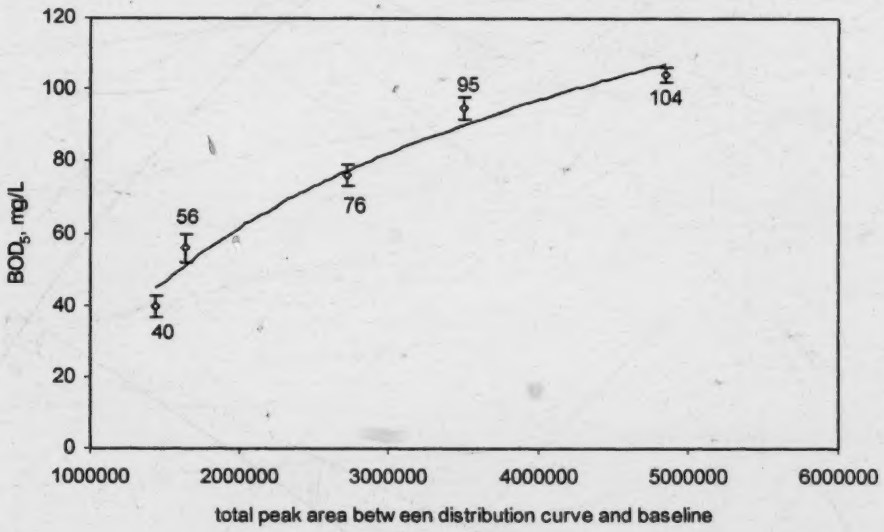

Figure 4.16 BOD_5 of each sample after ozonation versus its total peak area.

4.4 Conclusions

After membrane fractionation of the aged raw leachate, it was found that the metals were fractionated with the humic substances. Specifically, Co, Cr, Cu, Fe, Mo, Ni, Pb, Sb, Sn, Ti, and Zn were enriched in the samples of 0.45 μm to 10,000 Dalton and 10,000 to

5,000 Dalton; Ag, Al, As, Cd, Hg were enriched in the sample of 0.45 μm to 10,000 Dalton; V was enriched in the sample of 5,000 to 1,000 Dalton; and Bi was enriched in the sample of <1,000 Dalton.

The major COD and BOD_5 contributors were organic compounds with molecular weight less than 10,000 Dalton, while the major colour contributors were the organic compounds with molecular weight larger than 1,000 Dalton.

The addition of H_2O_2 had insignificant effect on the COD reduction for the samples of 10,000 to 5,000 Dalton and 5,000 to 1,000 Dalton. After oxidation with O_3 only or O_3/H_2O_2, more BOD_5 increase occurred for the samples of 10,000 to 5,000 Dalton and 5,000 to 1,000 Dalton.

Colour removal efficiency for the samples of aged raw leachate, 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; and 5,000 to 1,000 Dalton exceeded 87%. However, colour removal efficiency of the sample of <1,000 Dalton was 69% for O_3/H_2O_2 and 51% for O_3 only.

The addition of H_2O_2 enhanced the apparent reduction of the peaks with molecular weights larger than 1000 Dalton. The effect of H_2O_2 addition was more obvious for the samples of aged raw leachate, 0.45 μm to 10,000 Dalton and <1,000 Dalton; but insignificant for the samples of 10,000 to 5,000 Dalton and 5,000 to 1,000 Dalton, which is in agreement with the COD results.

There were no new peaks observed after oxidation with O_3/H_2O_2 for all the samples. After oxidation with O_3 only, new peaks with molecular weight less than 200 Dalton were observed in all of the samples except that of 0.45 μm to 10,000 Dalton. No correlation was found between the peak area of new peaks formed after oxidation and the

BOD_5 increase. The BOD_5 of each sample after oxidation with O_3 only was the logarithmic function of its total peak area between the molecular size distribution curve and its baseline.

4.5 References

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CHAPTER 5 AGED RAW LANDFILL LEACHATE: MEMBRANE FRACTIONATION, H_2O_2/UV OXIDATION AND MOLECULAR SIZE DISTRIBUTION ANALYSIS

5.1 Introduction

Hydroxyl radicals are the most powerful oxidant. Theoretically, oxygen-oxygen bond of H_2O_2 molecule is split under the UV radiation in the process of hydrogen peroxide with ultraviolet radiation (H_2O_2/UV), and two hydroxyl radicals (•OH) are formed. Therefore, H_2O_2/UV process is one of the effective advanced oxidation processes.

$$H_2O_2 + h\nu \rightarrow 2\ \bullet OH$$

In the past decade, several investigations have focused on the use of H_2O_2/UV oxidation to treat landfill leachates, mainly to reduce the refractory organic compounds in landfill leachates. The applications of H_2O_2/UV in landfill leachates are summarized in Table 5.1.

Table 5.1 shows: (1) The leachate oxidation with H_2O_2/UV usually was performed at pH below 4.0 to eliminate the scavengers of hydroxyl radicals (i.e., carbonate and bicarbonate); (2) The COD removal efficiency of H_2O_2/UV varied in a wide range from 22 to 90% depending on the leachate, pH, H_2O_2 dose, and UV fluence; (3) In most cases, medium- or high- pressure UV lamps were used in the H_2O_2/UV process, and H_2O_2 dose varied from 0.25 to 26.0 g H_2O_2/L leachate. It has been known that the leachate pH, H_2O_2 dose and UV fluence are three important factors that have influence on the treatment efficiency of the H_2O_2/UV process; however, the previous studies were performed at lowered pH (2.0 to 4.0), either H_2O_2 dose and UV fluence were investigated individually or

simultaneously. There is not a factorial experiment reported to investigate the relative importance of pH, H_2O_2 dose, and UV fluence to COD and colour reduction as well as BOD_5 increase.

Table 5.1 Applications of H_2O_2/UV in landfill leachate treatments.

COD, mg/L	BOD, mg/L	pH[a]	R_{COD}[b], %	BOD/COD[c]	UV, W	H_2O_2, g/L	Reference
760	NA	NA	22[d]	NA	150	3.4	Schulte et al. 1995
760	NA	3	99[e]	NA	150	3.4	Schulte et al. 1995
1,280	100	2	57	NA	100	NA	Ince 1998
1,280	100	2	59	NA	500	NA	Ince 1998
1,000 to 1,200	<10	3.0 to 4.0	90	NA	15	0.5	Steensen 1997
1,000 to 1,200	<10	3.0 to 4.0	85	NA	150	0.5	Steensen 1997
895	43	3.0 to 4.0	22	0.11	10[f]	0.25	Geenens et al. 1999
14,600[g]	2,920	3.0	79[h]	0.37	1,500	5.19	Qureshi et al. 2002
14,600[g]	2,920	3.0	91[h]	0.40	1,500	13.0	Qureshi et al. 2002
14,600[g]	2,920	3.0	96[h]	0.45	1,500	26.0	Qureshi et al. 2002

Notes:

[a]Optimum pH;

[b]Percentage of COD reduction;

[c]BOD/COD ratio after H_2O_2/UV treatment;

[d]With carbonate;

[e]Without carbonate;

[f]UV input in kW/m^3 leachate;

[g]TOC concentration of the raw leachate, the COD concentration of raw leachate was 26,000 mg/L;

[h]Removal efficiency of TOC.

For the H_2O_2/UV process, the suspended particle level and background absorbance will hinder the UV transmittance in leachate (Loge et al. 1999); therefore, the opportunity for UV to reach H_2O_2 will be reduced, and H_2O_2/UV process becomes less effective. However, the experimental data that can demonstrate the influence of suspended particle level on the H_2O_2/UV process are very limited. Up to date, no molecular size distribution of leachate after oxidation with H_2O_2/UV has been reported due to the difficulties caused by Bovine liver catalase for molecular size distribution analysis.

In this research, a 2^3 factorial experiment was performed using three factors: leachate pH, H_2O_2 dose, and UV fluence. The main objective of this experiment was to find the significant factors for COD and colour reduction and BOD_5 increase. Then, the aged raw leachate and membrane fractionated leachate samples were oxidized with H_2O_2/UV, and COD, BOD_5, colour, and molecular size distribution before and after oxidation were monitored. The influence of suspended particles on the leachate molecular size distribution was also investigated by oxidizing the raw leachates filtered with 0.8 μm and 0.45 μm, respectively, at the same condition as the aged raw leachate. This research will lead to a better understanding of the behaviour of humic substances and their effect on the performance of the H_2O_2/UV oxidation process.

5.2 Materials and methods

5.2.1 Landfill leachate

The aged raw leachate was collected from the equalization storage tank #2 at the Clover Bar Landfill Leachate Treatment Plant, Edmonton, Alberta, Canada. When the aged raw leachate sample was collected, the raw leachate had been stabilized in the equalization

storage tank for about one year due to the pipeline modification of the five-stage biological rotating contactors (RBCs). The volume and the average quality parameters of the aged raw leachate are shown in Table 5.2.

Table 5.2 Volume and average quality parameters of the aged raw leachate and the fractionated aged raw leachates.

Sample	Aged raw leachate	0.45μm to 10,000 Dalton	10,000 to 5,000 Dalton	5,000 to 1,000 Dalton	<1,000 Dalton
Volume, mL	5,000	1,000	1,478	1,300	2,220
UV absorbance 254 nm, cm^{-1}	0.917	0.474	1.416	0.659	0.348
COD, mg/L	1,090 ± 8	413 ± 0	1,130 ± 9	857 ± 13	633 ± 16
BOD_5, mg/L	27 ± 0	2 ± 0	16 ± 0	14 ± 3	12 ± 3
Colour, TCU	1,130 ± 7	1,280 ± 7	1,270 ± 7	341 ± 0	221 ± 7
NH_3-N, mg N/L	463 ± 0	96 ± 1	418 ± 5	412 ± 1	419 ± 0
Alkalinity, mg/L as $CaCO_3$	4,010 ± 7	1,040 ± 18	3,880 ± 14	3,730 ± 18	3,630 ± 18
pH	8.41 ±0.01	8.36 ± 0.01	8.32 ± 0.01	8.42 ± 0.01	8.36 ± 0.01

5.2.2 Membrane fractionation

The apparatus for membrane fractionation was the same as that illustrated in Figure 4.1, Chapter 4. The procedure for membrane fractionation is illustrated in Figure 5.1.

Five thousand (5,000) mL of aged raw leachate was filtered with 0.45 μm pore size filters, 42 mL was lost in 0.45μm pore size filters, and 4,958 mL filtrate was obtained. This filtrate was further fractionated with 10,000 MWCO membrane (PLGC, 10k, Millipore Corporation, Bedford, MA, catalogue #: CDUF001LG) at 124.2 kPa. After the fractionation, the pressure of membrane cell was released to zero and the inlet tubing and retentate tubing were taken out of the feed flask and put into a beaker containing 200 mL ultra pure water (conductivity^{-1}>18 MΩ). Then, the ultra pure water was run for 2 min to

wash out the organic compounds retained in membrane cell and after that, the pressure was increased to 124.2 kPa. The filtrate was also collected into the filtrate flask for 2 min. The retentate in the beaker was poured into the retentate flask, and the volumes of retentate and filtrate were measured with graduated cylinder. Then, the retentate was diluted to 1,000 mL with volumetric flask and formed the sample of 0.45μm to 10,000 Dalton to assure that the sample volume was large enough for the H_2O_2/UV oxidation experiments.

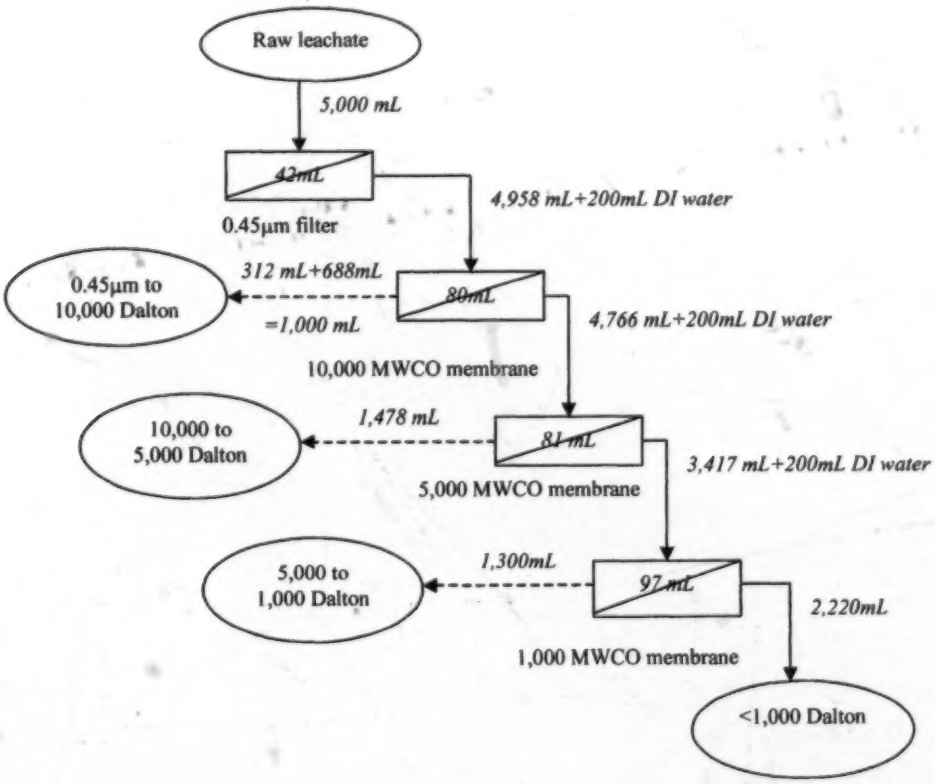

Figure 5.1 Schematic diagram of the membrane fractionation.

Figure 5.1 is very similar to Figure 4.2. Because they were two operations of membrane fractionation and two leachate samples, the volume and quality parameters of each fraction were different.

The process for the fractionation with 5,000 MWCO membrane (PLCC, 5k, Millipore Corporation, Bedford, MA, catalogue #: CDUF001LC) and 1,000 MWCO membrane (PLAC, 1k, Millipore Corporation, Bedford, MA, catalogue #: CDUF001LA) was the same as that of 10,000 MWCO membrane except that the retentate was not diluted. The volume and the average quality parameters of the four fractionated leachate samples before oxidation are also shown in Table 5.2.

5.2.3 Leachate oxidation

The experimental set-up for the leachate oxidation with H_2O_2/UV is depicted in Figure 5.2. A collimated beam apparatus with medium-pressure UV lamp (Calgon Carbon Corporation, model: PS1-1-120) was used for all the oxidation experiments. UV fluence rate at the sample surface was measured using a radiometer (Model: IL1400A, International Light, Inc., Newburyport, Massachusetts, USA).

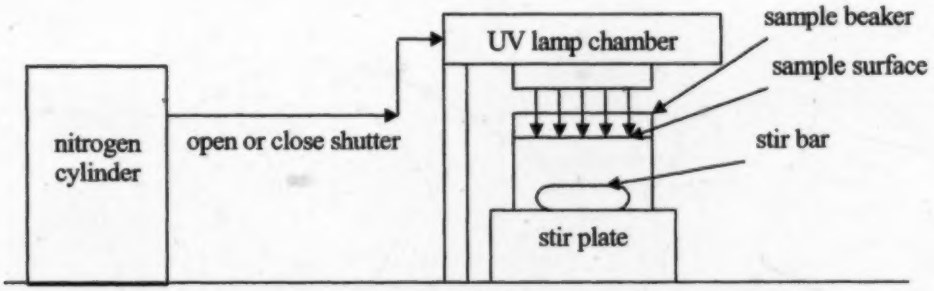

Figure 5.2 Experimental set-up for H_2O_2/UV oxidation.

A 2^3 factorial experiment was performed on the aged raw leachate with H_2O_2/UV process to investigate the leachate pH, H_2O_2 dose and UV fluence on the COD and colour reduction as well as the BOD_5 increase; then the aged raw leachate, fractionated aged raw leachates and the aged raw leachates filtered with 0.45 μm and 0.8 μm, respectively, were

oxidized with H_2O_2/UV. The design matrix for the 2^3 factorial experiment is shown in Table 5.3. The measured responses for the factorial experiment were COD, BOD_5 and colour. The conditions for sample oxidation with H_2O_2/UV are shown in Table 5.4.

Table 5.3 Design matrix of the factorial experiment for aged raw leachate oxidation with H_2O_2/UV, and COD, BOD_5 and colour after oxidation.

Trial #	Sequence of trial	H_2O_2 dose g/L	UV fluence t J/cm^2	pH	V_{sample} mL	COD mg/L	BOD_5 mg/L	Colour CTU
1	No. 2	5.02	32.0	8.40	250	890 ± 10	71 ± 4	170 ± 5
2	No. 3	2.51	32.0	8.40	250	917 ± 4	68 ± 1	225 ± 5
3	No. 1	5.02	16.0	8.40	250	936 ± 4	53 ± 5	262 ± 5
4	No. 4	2.51	16.0	8.40	250	944 ± 11	56 ± 6	343 ± 5
5	No. 6	5.02	32.0	6.0	250	848 ± 10	74 ± 1	195 ± 0
6	No. 5	2.51	32.0	6.0	250	898 ± 4	68 ± 2	229 ± 5
7	No. 8	5.02	16.0	6.0	250	909 ± 4	61 ± 6	288 ± 10
8	No. 7	2.51	16.0	6.0	250	938 ± 0	53 ± 4	369 ± 10

Note: 1.0 mL of Bovine liver catalase solution at 2.0 mg/mL was added to each sample after oxidation.

Table 5.4 Oxidation conditions for the aged raw leachate, fractionated leachate samples and filtered leachate samples with 0.8 μm and 0.45 μm filters respectively with H_2O_2/UV.

Sample	Treatment pH	UV fluence t, J/cm^2	H_2O_2 dose, g/L	V_{sample}, mL
Aged raw leachate	4.50	30.6	5.02	250
Aged raw leachate <0.8 μm	4.50	30.6	5.02	250
Aged raw leachate < 0.45 μm	4.50	30.6	5.02	250
0.45μm to 10,000 Dalton	4.50	30.6	5.02	250
10,000 to 5,000 Dalton	4.50	38.3	7.54	250
5,000 to 1,000 Dalton	4.50	30.6	5.02	250
<1,000 Dalton	4.50	30.6	5.02	250

Notes: 3.0 mL of Bovine liver catalase solution at 2.0 mg/mL was added to each sample after the pH was adjusted back to 6 to 7.

5.2.4 Analytical methods

UV absorbance of each leachate sample was read with a 10-mm cuvette at the wavelength of 254 nm. COD, BOD_5, and colour were determined following the Standard Methods (American Public Health Association et al. 1998). Specifically, COD was determined in triplicate; BOD_5 and colour were measured in duplicate, and the absorbance of colour was read at 460 nm. COD and BOD_5 of Bovine liver catalase solution were measured together with leachate samples. In this way, the positive errors of COD and BOD_5 caused by Bovine liver catalase were corrected.

Molecular size distribution analysis was performed with HPLC (Shimadzu Corporation, Japan) equipped with PW_{XL} guard column (Supelco/Sigma-Aldrich Canada, catalogue #: 808033, 40 mm × 6.0 mm, 12 μm particle size), $G3000PW_{XL}$ gel filtration column (Supelco/Sigma-Aldrich Canada, catalogue #: 808021, 300 mm × 7.8 mm, 6 μm particle size), and UV detector at 254 nm. The data acquisition system for the HPLC was Shimadzu Class-VP. Ten (10) mM NaCl solution filtered with 0.45 μm pore size filter was used as eluant at a flow rate of 0.5 mL/min. The analytical column was calibrated with PEG size standard solution as shown in Figure 3.10 in Section 3.2.4.3.4, Chapter 3.

To eliminate the adverse influence of Bovine liver catalase on the gel filtration column, the samples were centrifuged by using Ultrafree®-CL High-flow Biomax-PB centrifugal filter units (Sigma-Aldrich Canada, catalogue #: M2286) with 100,000 Dalton nominal molecular weight limit (NMWL) PTHK polyethersulfone membrane before injection. The centrifuge was run at 3,000 rpm for 10 min.

Linear regression analysis was used to calculate the effects and interactions between

the different factors considered in the factorial experiment. Normal score plots were used to estimate the experimental error.

The calculation matrix for COD is shown in Table 5.5. COD values were used for the input *Y* range, and matrix (H_2O_2, 1) to (H_2O_2*t*pH, 8) was used as input *X* range, where t was the UV fluence. A 95% confidence level was used for the linear regression analysis. In the output of the linear regression, variables 1 to 7 corresponded to H_2O_2, t, pH, H_2O_2*t, H_2O_2*pH, t*pH, and H_2O_2*pH. The average on the regression sheet corresponded to the average COD. The values of the effects and interactions were obtained from the absolute values of the coefficients of variables 1 to 7 multiplied by 2, respectively. Assuming the values of the effects or interactions had occurred simply as a result of random variation about a constant mean, and the changes in levels of the variables had no real effect at all on the percent conversion. Then the effects would have been roughly normal and have been distributed about zero (Box et al. 1978). The absolute values of the effects or interactions were placed in an order, and the letter "*i*" denoted the order number. The calculated results of the probability "*P*" and normal score NORMSINV (*P*) are shown in Table 5.6.

Table 5.5 Effects and interactions calculation matrix for COD.

Trial #	H_2O_2	t	pH	H_2O_2*t	H_2O_2*pH	t*pH	H_2O_2*t*pH	COD, mg/L
1	-1	-1	-1	1	1	1	-1	890 ± 10
2	1	-1	-1	-1	-1	1	1	917 ± 4
3	-1	1	-1	-1	1	-1	1	936 ± 4
4	1	1	-1	1	-1	-1	-1	944 ± 11
5	-1	-1	1	1	-1	-1	1	848 ± 10
6	1	-1	1	-1	1	-1	-1	898 ± 4
7	-1	1	1	-1	-1	1	-1	909 ± 4
8	1	1	1	1	1	1	1	938 ± 0

Note: t was UV fluence.

Table 5.6 Calculation of the normal probabilities and normal scores.

Parameter	Identification	H_2O_2	t	pH	H_2O_2*t	H_2O_2*pH	t*pH	H_2O_2*t*pH
COD	Effects/interactions	28.6	43.1	23.6	9.9	10.9	6.8	0.5
	Order number *i*	6	7	5	3	4	2	1
	$P = 100\ (i\text{-}0.5)/7$	0.786	0.929	0.643	0.357	0.500	0.214	0.071
	NORMSINV *(P)*	0.79	1.47	0.37	-0.37	0.00	-0.79	-1.47
BOD_5	Effects/interactions	3.5	14.5	1.9	0.7	3.2	0.4	2.2
	Order number *i*	6	7	3	2	5	1	4
	$P = 100\ (i\text{-}0.5)/7$	0.786	0.929	0.357	0.214	0.643	0.071	0.500
	NORMSINV *(P)*	0.79	1.47	-0.37	-0.79	0.37	-1.47	0.00
Colour	Effects/interactions	62.7	110.6	20.3	18.4	5.5	5.5	5.5
	Order number *i*	6	7	5	4	3	2	1
	$P = 100\ (i\text{-}0.5)/7$	0.786	0.929	0.643	0.500	0.357	0.214	0.071
	NORMSINV *(P)*	0.79	1.47	0.37	0.00	-0.37	-0.79	-1.47

The normal scores of the probability for BOD_5 and colour were obtained by using the same procedure. On the normal score plot, the smaller unimportant effects/interactions should distribute around a straight line, and these unimportant effects/interactions in the same magnitude as the experimental error. The important effects/interactions should fall away from the straight line defined by the smaller unimportant effects/interactions.

5.3 Results and discussion

5.3.1 Factorial experiment on aged raw leachate oxidation with H_2O_2/UV

The normal score plots for the effects/interactions on COD, BOD_5 and colour are shown in Figures 5.3 to 5.5.

The significant factors for COD reduction include UV fluence, H_2O_2 dose, and pH (Figure 5.3). UV fluence was the significant factor for BOD_5 improvement among these three tested factors (Figure 5.4). The significant factors for colour reduction include UV

fluence and H_2O_2 dose (Figure 5.5), and pH did not play a significant role for colour reduction.

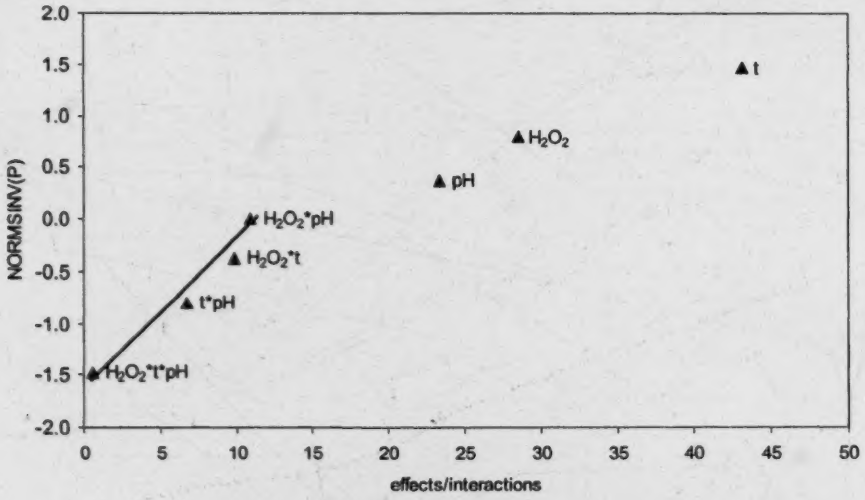

Figure 5.3 Normal score plot for COD.

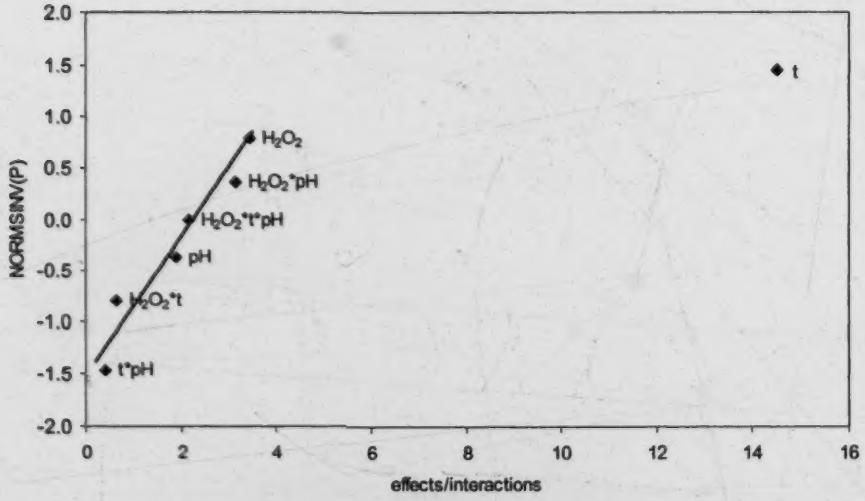

Figure 5.4 Normal score plot for BOD_5.

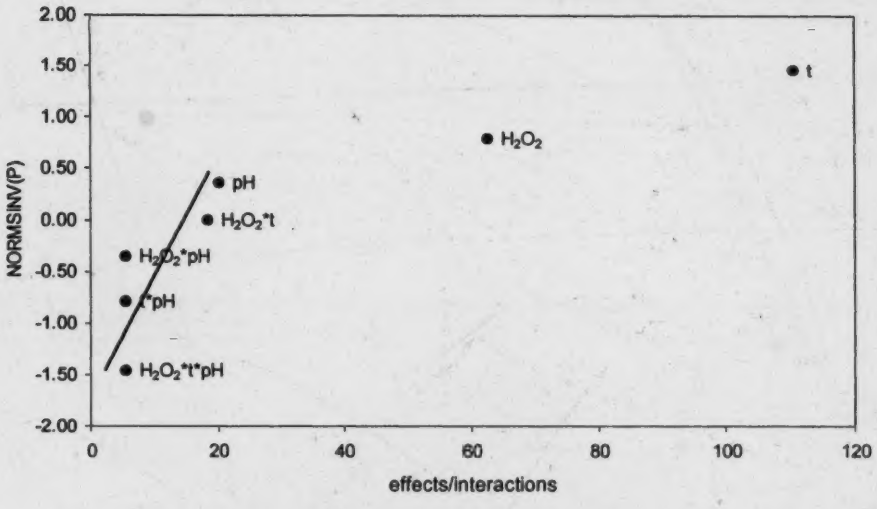

Figure 5.5 Normal score plot for colour.

5.3.2 H_2O_2/UV oxidation of membrane fractionated leachate samples and aged raw leachate

5.3.2.1 Chemical oxygen demand (COD)

Figure 5.6 depicts the COD of leachate samples before and after oxidation with H_2O_2/UV. The removed COD by H_2O_2/UV treatment of aged raw leachate, 0.45 μm to 10,000 Dalton, 10,000 to 5,000 Dalton, 5,000 to 1,000 Dalton, and <1,000 Dalton samples are 239, 128, 269, 279, and 74 mg/L. Although the higher H_2O_2 dose and larger UV fluence were applied to the sample of 10,000 to 5,000 Dalton (Table 5.4), the removed COD of this sample did not increase compared to the sample of 5,000 to 1,000 Dalton. Both samples had neither particles nor hydroxyl radical scavengers (pH = 4.50, carbonate and bicarbonate had been removed). The ineffectiveness of the higher H_2O_2 dose and larger UV fluence to the sample of 10,000 to 5,000 Dalton might be caused by its background UV absorbance (1.416 cm^{-1}). For the sample of 10,000 to 5,000 Dalton, it is likely that the same

amount of hydroxyl radicals were produced with the high H_2O_2 dose and large UV fluence as those in the sample of 5,000 to 1,000 Dalton, therefore, almost the same amount of COD was removed.

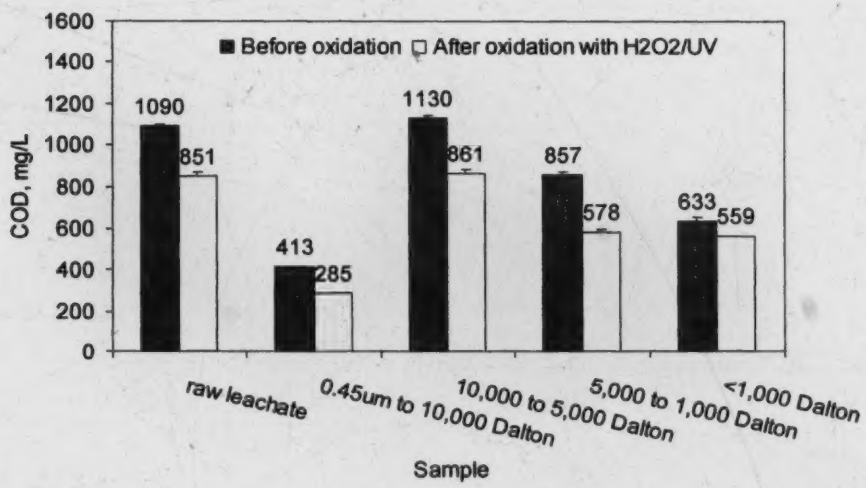

Figure 5.6 COD before oxidation and after oxidation with H_2O_2/UV at treatment pH = 4.50.

Another important factor for the UV-related processes was the concentration of suspended particles in the leachate (Loge et al. 1999). Those suspended solids can limit the UV transmittance in the leachate. All of the samples, except the aged raw leachate, were filtered with 0.45 μm pore size membrane. Thus, those samples became particle-free. However, the removed COD was 239 mg/L and 279 mg/L for the aged raw leachate and the sample of 5,000 to 1,000 Dalton. The UV absorbances of the aged raw leachate and the sample of 5,000 to 1,000 Dalton were 0.917 cm^{-1} and 0.659 cm^{-1}, respectively. Unfortunately, it is unknown the difference in the COD reduction for both samples was caused by the UV absorbance or the particles in the aged raw leachate.

To investigate the influence of particles on the COD reduction, the aged raw leachate filtered with 0.8 μm filter (raw leachate < 0.8 μm) and 0.45 μm filter (raw leachate < 0.45 μm) were oxidized with H_2O_2/UV at the same oxidation conditions used on the aged raw leachate (Table 5.4), respectively. The results are shown in Figure 5.7.

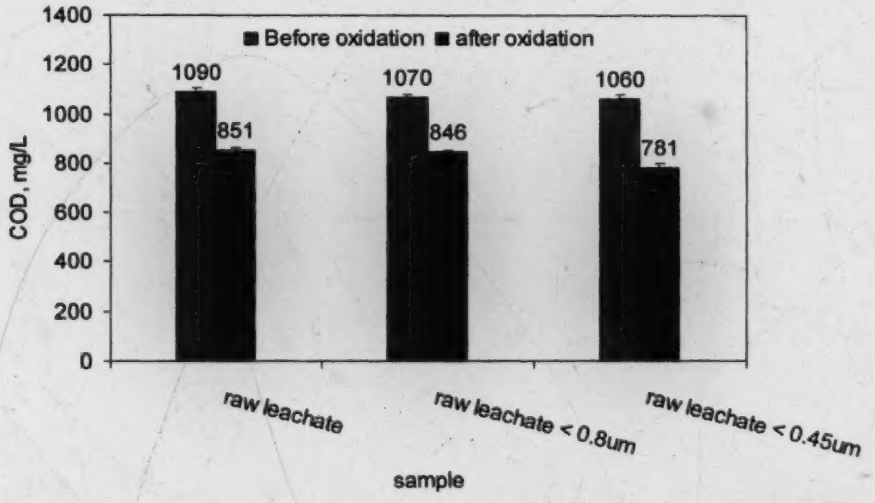

Figure 5.7 Effect of particles on COD reduction of H_2O_2/UV at treatment pH = 4.50.

It was found that the COD reduction of raw leachate, raw leachate < 0.8 μm and raw leachate < 0.45 μm was 239 mg/L, 226 mg/L and 279 mg/L. At a 95% confidence level, there was no significant difference between 239 mg/L and 226 mg/L of COD reduction; however, there was significant difference between 226 mg/L and 279 mg/L. In other words, after oxidation with H_2O_2/UV, the COD reduction of raw leachate was almost equal to the COD reduction of raw leachate < 0.8 μm, and COD reduction of raw leachate < 0.45 μm was significantly larger than those of the aged raw leachate and the raw leachate <0.8 μm. Therefore, the difference between the COD reductions of raw leachate and raw leachate < 0.45 μm might be considered as the influence of particles in the leachates.

5.3.2.2 Five-day biochemical oxygen demand (BOD_5)

Figure 5.8 shows the BOD_5 before and after oxidation with H_2O_2/UV. After oxidation with H_2O_2/UV, the BOD_5 increase for the aged raw leachate, 0.45 μm to 10,000 Dalton, 10,000 to 5,000 Dalton, 5,000 to 1,000 Dalton, and <1,000 Dalton samples, was 43, 44, 74, 75, 79 mg/L, respectively. Therefore, H_2O_2/UV process was quite effective for the BOD improvement.

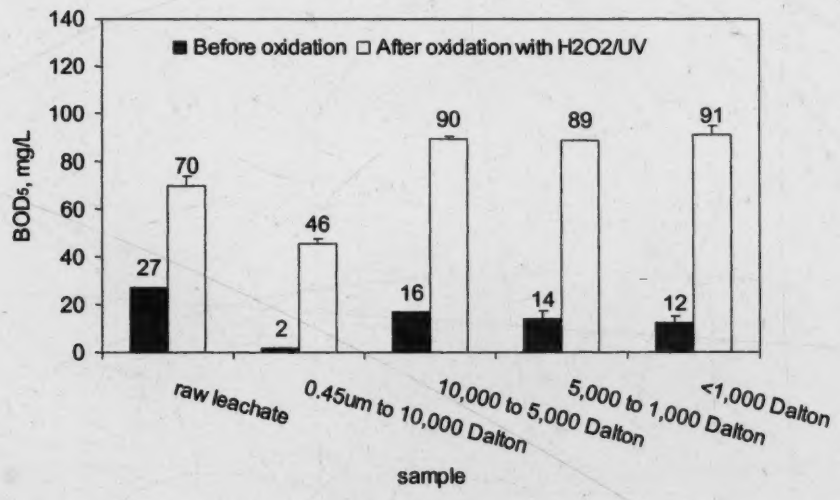

Figure 5.8 BOD_5 before oxidation and after oxidation with H_2O_2/UV at treatment pH = 4.50.

In the factorial experiment, UV fluence was the significant factor that affected the BOD_5 improvement. The BOD_5 of the fractions of 10,000 to 5,000 Dalton, 5,000 to 1,000 Dalton and <1,000 Dalton after H_2O_2/UV oxidation was very close to each other. These results seemed to be consistent with the conclusion about the BOD_5 that was drawn from the factorial experiment. The larger UV fluence applied to the sample of 10,000 to 5,000 Dalton did not increase the BOD_5 improvement compared to the samples of 5,000 to 1,000

Dalton and <1,000 Dalton. Such result might indicate when the UV fluence reached a certain level (for example, 30.6 J/cm^2), the larger UV fluence above this level may not to able to produce more BOD_5.

Compared to the BOD_5 of the fractions of 10,000 to 5,000 Dalton, 5,000 to 1,000 Dalton, and <1,000 Dalton after H_2O_2/UV oxidation, the BOD_5 of aged raw leachate increased by a smaller extent. This BOD_5 difference between the aged raw leachate and the fractionated samples might be attributed to the influence of the suspended particles in the aged raw leachate.

The BOD_5 before and after oxidation with ozone only is shown in Figure 5.9.

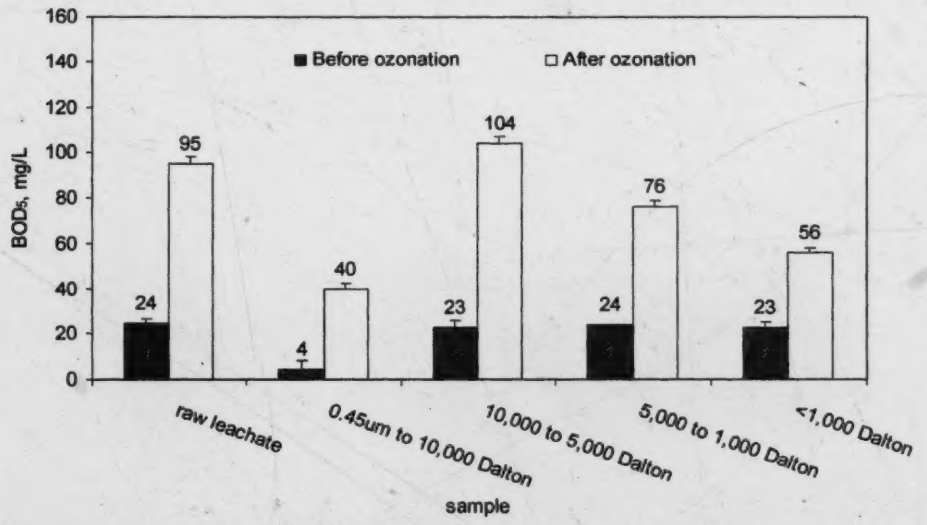

Figure 5.9 BOD_5 before and after oxidation with O_3 only at treatment pH in the range of 8.29 to 8.55 (from Chapter 4).

Comparing Figures 5.8 and 5.9 clearly indicates that the BOD_5 of each sample after oxidation with H_2O_2/UV was different from the BOD_5 after ozonation treatment. A commonly accepted viewpoint about the BOD_5 improvement after ozonation is that the

BOD_5 improvement is due to the ozone partial oxidation (Langlais et al. 1991; Langlais et al. 1989; Beltran-Heredia et al. 2000; Baig and Liechti, 2001; Geenens et al. 2001). This partial oxidation is believed to cause the cleavage of double bonds and/or aromatic structures, and form small molecular biodegradable intermediate products. The BOD_5 improvement after H_2O_2/UV oxidation seems to be caused by other mechanisms that need further exploration.

5.3.2.3 Colour

Figure 5.10 depicts the colour intensity of each sample before and after oxidation with H_2O_2/UV. Colour removal efficiency was 65%, 96%, 95%, 94% and 85% for the aged raw leachate, 0.45 μm to 10,000 Dalton, 10,000 to 5,000 Dalton, 5,000 to 1,000 Dalton and <1,000 Dalton samples, respectively. Therefore, colour of the samples filtered with 0.45 μm pore size membrane were reduced effectively with H_2O_2/UV.

The low colour removal efficiency of the aged raw leachate might be caused by the particles in this sample since the particles in the sample limited the UV transmittance in the sample (Loge et al. 1999), thereby reducing the opportunity of UV to react with H_2O_2. The higher H_2O_2 dose and larger UV fluence did not appear to make any positive contribution to the colour reduction for the fraction of 10,000 to 5,000 Dalton.

The chromophores in the humic substances causing yellow colour and brown colour include quinonoid structures (Gore et al. 1962) and/or azo structures (Hao et al. 2000). These functional groups contain either benzene rings or nitrogen-to-nitrogen double bonds, or both. Two reasons might cause the colour reduction: first, the quinonoid structures and azo structures might easily absorb UV radiation and were cleaved; therefore, the colour was reduced. Second, the colour might be reduced by •OH radicals since the factorial

experiment showed that both UV fluence and H_2O_2 dose were important for colour reduction.

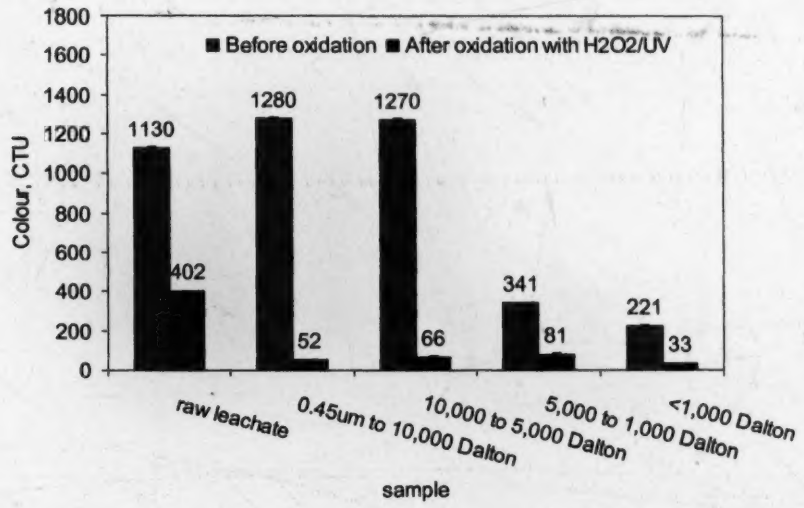

Figure 5.10 Colour before oxidation and after oxidation with H_2O_2/UV at treatment pH = 4.50.

5.3.2.4 Ratios of COD removed, colour removed and BOD_5 increased to UV fluence

The ratios of COD removed, colour removed and BOD_5 increased to the UV fluence, after H_2O_2/UV oxidation, are the important economical factors for evaluating the cost and effectiveness of the process. These are shown in Figure 5.11.

The sample of 5,000 to 1,000 Dalton had the highest ratio of COD removed to the UV fluence. For the sample of 10,000 to 5,000 Dalton, the ratio of COD removed to UV fluence did not appear to be improved by the higher H_2O_2 dose and larger UV fluence. It is postulated that the high UV absorbance interfered with the interaction between UV and H_2O_2, thus reducing the formation of •OH radicals. Therefore, the higher UV fluence did

not increase the COD reduction for the sample of 10,000 to 5,000 Dalton, but resulted in a low ratio of COD removed to UV fluence.

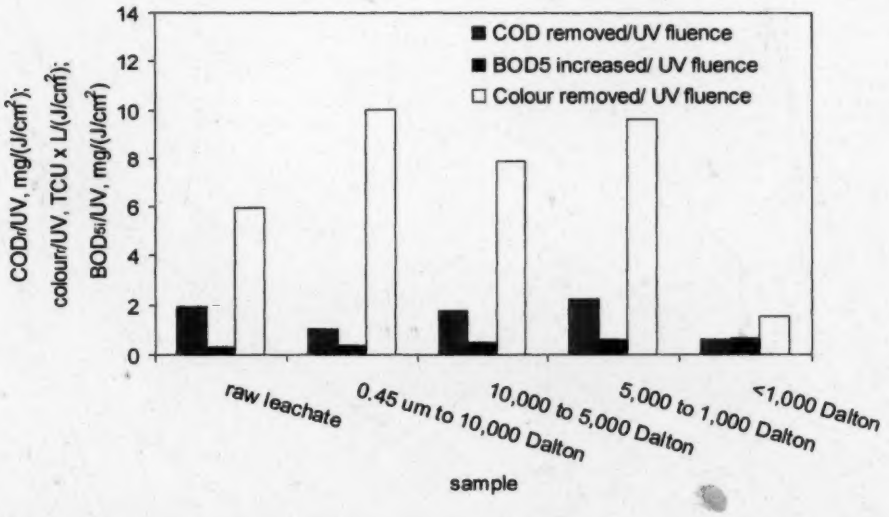

Figure 5.11 COD removed, colour removed and BOD_5 increased to UV fluence at treatment pH = 4.50.

The samples of 5,000 to 1,000 Dalton and < 1,000 Dalton had the highest ratios of BOD_5 increased to UV fluence, thus having higher energy utilizing efficiencies. For the sample of 10,000 to 5,000 Dalton, BOD_5 increase after oxidation was almost equal to those of the sample of 5,000 to 1,000 Dalton and < 1,000 Dalton, but a higher UV fluence was applied to this sample. Consequently, a lower BOD_5 increased to UV fluence (i.e., a poor energy utilizing efficiency) was produced.

The high ratios of colour removed to UV fluence were obtained for all of the samples except the sample of <1,000 Dalton. The low ratio of colour removed to UV fluence of the sample of <1,000 Dalton was due to the absolute amounts of initial colour and removed colour of this sample being low. When this sample was subjected to H_2O_2/UV

treatment, it might be because this sample did not have so many colour-causing substances to be oxidized by H_2O_2/UV or because the colour-causing substances were not easy to be oxidized by H_2O_2/UV.

Compared to other samples with high ratio of colour removed to UV fluence, the ratio of colour removed to UV fluence of the sample of 10,000 to 5,000 Dalton was relatively low. This was because the high UV fluence was applied to this sample.

5.3.2.5 Molecular size distribution

Figures 5.12 to 5.16 are the molecular size distributions before and after oxidation with H_2O_2/UV for the samples of the aged raw leachate; 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton; and <1,000 Dalton, respectively.

All of the peaks with molecular weight between 6,730 to 300 Dalton were reduced after oxidation with H_2O_2/UV, and no new peaks were observed for the samples except that of 0.45 μm to 10,000 Dalton. A new peak with molecular weight of 1,720 Dalton was observed in the sample of 0.45 μm to 10,000 Dalton after H_2O_2/UV oxidation, however, it was unknown whether it was an oxidation by-product or the leftover of the right shoulder of the peak with molecular weight of 3,710 Dalton.

As mentioned in Section 5.3.2.1, the molecular size distributions of the samples of the aged raw leachate, raw leachate <0.8 μm and raw leachate <0.45 μm after oxidation and the molecular size distribution of aged raw leachate before oxidation are shown in Figure 5.17. After oxidation with H_2O_2/UV, the aged raw leachate < 0.8 μm had almost the same molecular size distribution as the aged raw leachate after oxidation (i.e., both curves overlapped on each other). Compared to the aged raw leachate and the aged raw leachate < 0.8μm, the peaks of large molecules of the aged raw leachate < 0.45 μm was reduced more.

These results demonstrated the extent of the suspended particles affecting the reduction of the molecules during the H_2O_2/UV process.

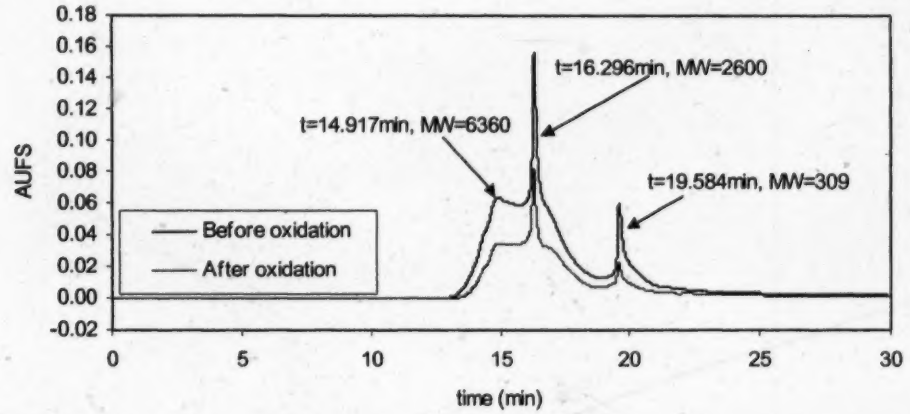

Figure 5.12 Molecular size distributions of the aged raw leachate before and after oxidation with H_2O_2/UV at treatment pH = 4.50.

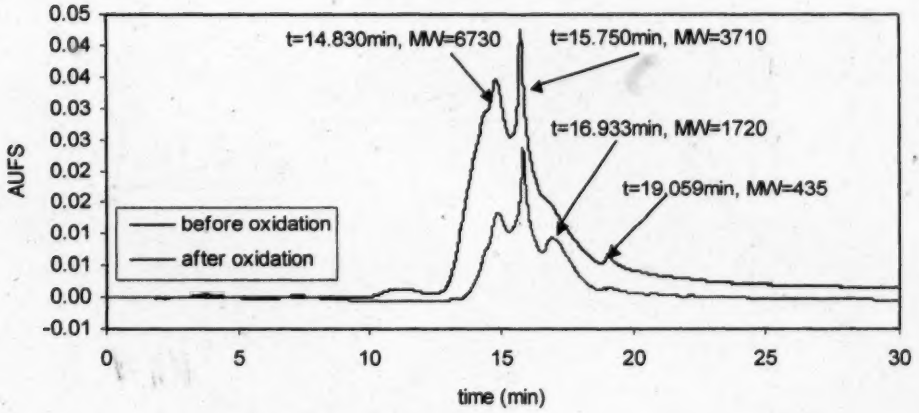

Figure 5.13 Molecular size distributions of 0.45 μm to 10,000 Dalton before and after oxidation with H_2O_2/UV at treatment pH = 4.50.

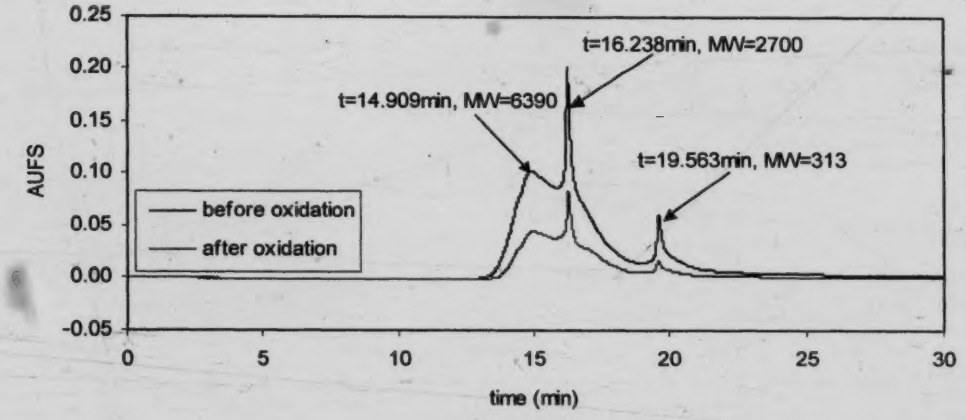

Figure 5.14 Molecular size distributions of 10,000 to 5,000 Dalton before and after oxidation with H_2O_2/UV at treatment pH = 4.50.

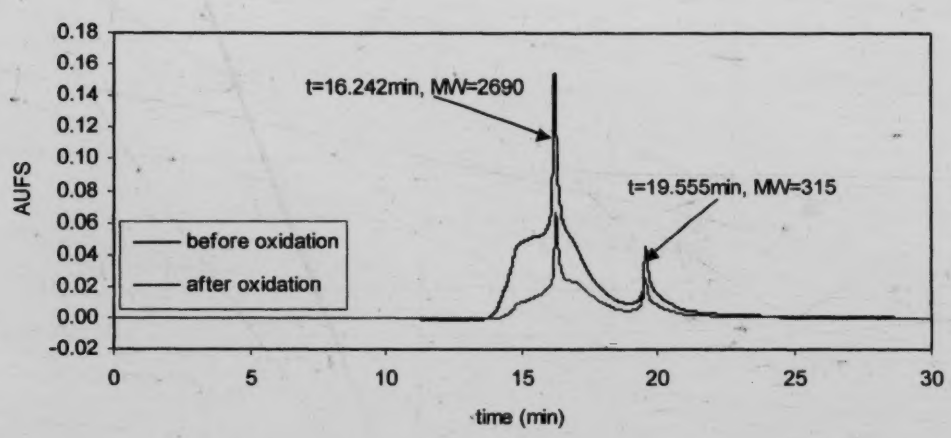

Figure 5.15 Molecular size distributions of 5,000 to 1,000 Dalton before and after oxidation with H_2O_2/UV at treatment pH = 4.50.

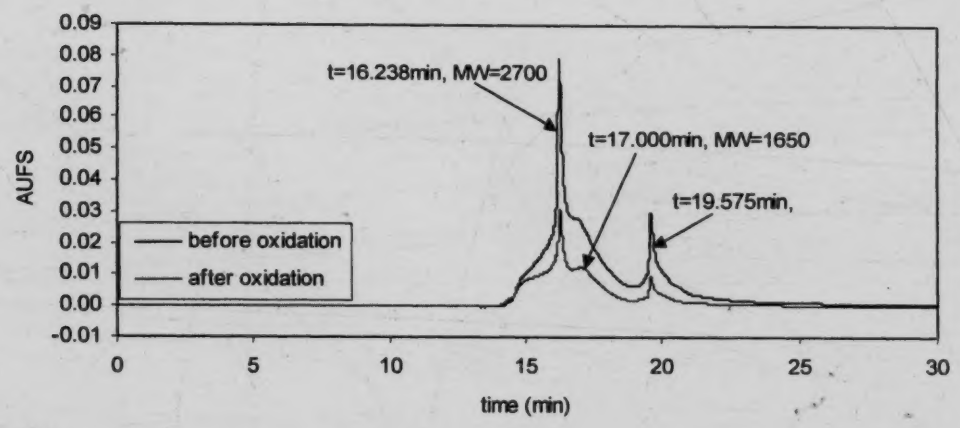

Figure 5.16 Molecular size distributions of <1,000 Dalton before and after oxidation with H_2O_2/UV at treatment pH = 4.50.

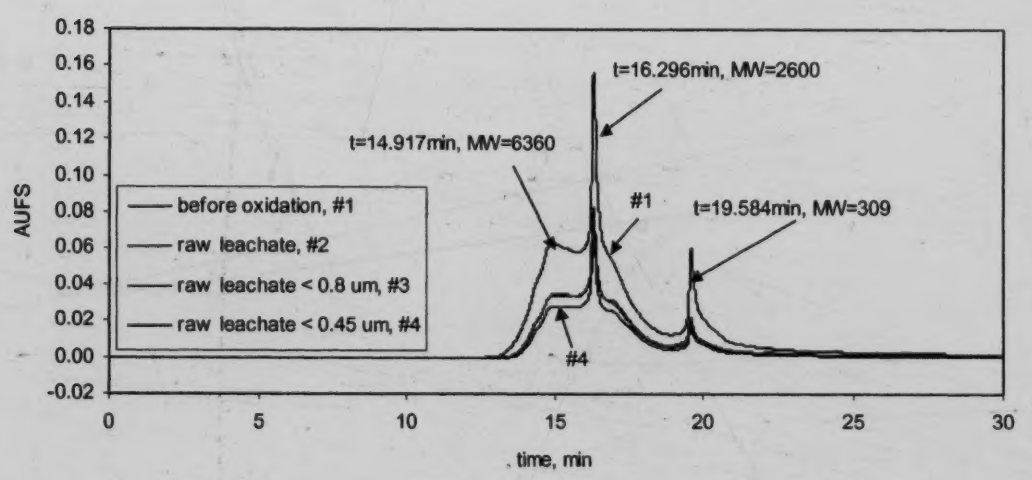

Figure 5.17 Molecular size distributions of raw leachates with different suspended particle levels after H_2O_2/UV at treatment pH = 4.50.

5.4 Conclusions

A 2^3 factorial experiment with the leachate pH, H_2O_2 dose, and UV fluence, as the factors, was performed. The measured responses were COD, BOD_5 and colour. Additionally, the fractionated aged raw leachate samples as well as aged raw leachate sample were oxidized with H_2O_2/UV at pH = 4.50. COD, BOD_5, colour and molecular size distribution were determined before and after oxidation. The following conclusions were drawn from this research:

1. In the H_2O_2/UV process for the aged raw leachate oxidation, the significant factors for COD reduction were UV fluence, H_2O_2 dose and leachate pH. UV fluence was the significant factor for BOD_5 improvement. Meanwhile, the significant factors for colour reduction were UV fluence and H_2O_2 dose.
2. After H_2O_2/UV treatment at pH = 4.50, the COD reduction of the aged raw leachate and the fractionated aged raw leachates varied from 74 to 279 mg/L, and the particles larger than 0.45 μm hindered the COD reduction. Compared to the aged raw leachate (containing particles), the BOD_5 of fractionated aged raw leachates (particle-free) increased more; H_2O_2/UV treatment effectively reduced colour for the fractionated aged raw leachates, but it was less effective for the colour reduction of the aged raw leachate (containing particles).
3. Molecular size distribution analysis demonstrated that no new peaks were observed for the samples except that of 0.45 μm to 10,000 Dalton. For the sample of 0.45 μm to 10,000 Dalton, the new peak with molecular weight of 1,720 Dalton may be either the oxidation by-products or the leftover of the organic compounds that could not be oxidized by H_2O_2/UV treatment. Molecular size distribution analysis also

indicated that the particles larger than 0.45 μm in the aged raw leachate samples had adverse influence on the reduction of the large molecule peaks in the H_2O_2/UV process.

5.5 References

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CHAPTER 6 OZONATION OF AGED RAW LANDFILL LEACHATE AND BIOLOGICALLY TREATED LANDFILL LEACHATE [4]

6.1 Introduction

The major fraction of the organic compounds in the biologically treated landfill leachate is the large refractory organic compounds, i.e., humic substances (Chian 1977; Lecoupannec 1999). In the past decade, ozonation has been widely used either to oxidize large refractory organic compounds in landfill leachate to water, carbon dioxide and other end-products, or to break them into small molecular compounds, which may be removed in a subsequent biological treatment system. Table 6.1 presents the summary of ozonation of the biologically treated landfill leachates and refractory raw landfill leachates during a number of studies.

Table 6.1 shows the following facts: (1) The ozonation of landfill leachates was conducted within the pH range of 7.0 to 8.5; (2) The COD removal efficiency varied from 25% to 80%, and more than 1.5 g O_3 was required to remove 1 g of COD in most cases; (3) Colour removal efficiency ranged from 52% to 90%; (4) Compared to COD removal, a small amount of O_3 was required to remove the same percentage of colour; and (5) After ozonation, ratio of BOD_5/COD was improved to above 0.1 (i.e., the biodegradability of the leachate has been improved after ozonation).

Regarding the biodegradability increase, the popular viewpoint is that the large refractory organic compounds are broken down to smaller more biodegradable oxidation

[4] A version of this chapter has been submitted for publication. Wang, F., Gamal El-Din, M. and Smith, D. W., *Environmental Technology* (March 2004).

by-products, thereby leading to the biodegradability improvement (Langlais et al. 1989; Langlais et al. 1991; Beltran-Heredia et al. 2000; Baig and Liechti 2001; Geenens et al. 2001). However, more experimental data are needed to support this viewpoint.

Imai et al. (1998) observed the molecular size distributions of a refractory raw landfill leachate before and after ozonation using an HPLC equipped with a gel filtration column and a UV detector operated at 254 nm. The eluant was 0.3 M NaCl in 0.1 M phosphate buffer, and its flow rate was 0.8 mL/min. It was found that the peaks that represented large molecules were reduced after ozonation for 3 hours. The peak formation caused by small molecules was observed at elution time from 17 to 21 min. However, it was unknown if these peaks were the oxidation by-products of large molecules or the leftover of some organic compounds, which had the same molecular weights, since these peaks were under the right shoulder of the leachate molecular size distribution obtained before ozonation. Meanwhile, Imai et al. (1998) found that the fractions eluted within 19 to 23 min were the major dissolved organic carbon (DOC) contributors. Wang et al. (2004) investigated the molecular size distribution changes of an aged raw leachate after being ozonated at different used-ozone doses. They observed the formation of ozonation by-products, nevertheless, there was no correlation observed between ozonation by-products and the BOD_5 increase.

In this research, the RBC effluent was oxidized with ozone at different used-ozone doses. COD, BOD_5, and colour were determined before and after treatment. The relationships of COD, BOD_5, and ratio of BOD_5/COD as functions of the used-ozone dose were established. The molecular size distributions of the RBC effluent at different used-ozone doses were analyzed with an HPLC equipped with a gel filtration column and a UV

detector. The molecular size distributions of RBC effluent would help in understanding the refractory landfill leachate treatments. The relationships between used-ozone dose, COD, BOD_5 and ratio of BOD_5/COD as functions of the total peak area, between the molecular size distribution curve and its baseline, were established. These relationships may be useable for online ozonation treatment process control as well as predicting the treatment efficiencies for COD, BOD_5 and the ratio of BOD_5/COD.

Table 6.1 Ozonation of biologically treated and refractory raw landfill leachates.

COD mg/L	BOD mg/L	NH_3-N mg/L as N	Alkalinity mg/L as $CaCO_3$	pH	R_{COD}[a] %	R_{colour}[b] %	BOD/COD[c]	O_3/COD[d] g/g	Reference
Biologically treated landfill leachates									
2,300	210	564	4,160	8.0	62	NA	NA	1.5	Bigot et al. 1994
2,300	210	564	4,160	8.0	NA	90	NA	0.75	Bigot et al. 1994
300 to 1,200	<10	<5	600 to 2,800[e]	7.0 to 8.0	80	NA	NA	3.0[f]	Steensen 1997
500	30	NA	NA	7.0	NA	NA	140 mg/L[g]	34[h]	Karrer et al. 1997
460	8.4	370[i]	NA	NA	71	NA	NA	1.8	Barratt et al. 1997
1,070	14.4	67[i]	NA	8.5	67	NA	NA	1.7	Barratt et al. 1997
3,500	25	470	NA	8.2	67	NA	0.21	0.7[j]	Derco et al. 2002
Refractory raw landfill leachates									
4,000	230	NA	NA	8.5	25	90	NA	0.53	Sandya et al. 1995
151[k]	5	177	NA	8.1	33	NA	0.35	NA	Imai et al. 1998
895	43	626	703	8.2	30	NA	0.11	1.5	Geenens et al. 2001
25,950	2,920	1,854	12,280	7.8	56	52	0.32	3.1[l]	Qureshi et al. 2002
1,090	39	455	4,030	8.30	37	92	0.136	2.4[m]	Wang et al. 2004

Notes:

NA: not available.

[a]COD removal efficiency;

[b]Colour removal efficiency;

[c]BOD/COD after oxidation treatment;

[d]Ratio of O_3/COD is the mass of ozone in inlet gas to the mass of the initial COD, unless indicated;

[e]Alkalinity as HCO_3^-;

[f]Ratio of mass of ozone consumed to mass of COD eliminated;

[g]BOD_5 after ozonation;

[h]Applied-ozone dose in mg O_3/L leachate;

[i]Total nitrogen

[j]Mass of ozone consumed to mass of initial COD;

[k]COD_{Mn} (chemical oxygen demand determined with potassium permanganate, $KMnO_4$);

[l]Ratio of TOC removed to O_3.

[m]Mass of used-ozone to initial mass of COD.

6.2 Experimental methods and materials

6.2.1 Landfill leachate

Clover Bar Landfill Site has been accepting solid waste since 1975, and the expected closure date for this landfill site will be in 2006 or later. The treatment processes at the Clover Bar Landfill Leachate Treatment Plant include physical/chemical and biological treatment processes. The aged raw leachate was taken from the equalization storage tank 2#. When the aged raw leachate was collected, it had been stabilized in the equalization storage tank for about one year due to the pipeline modification for the RBC system. After RBC system restart-up for three months, the RBC effluent was collected

from the supernatant of the secondary clarifier of the RBCs. Table 6.2 shows the quality parameters and their standard deviations of the aged raw leachate and the RBC effluent.

Table 6.2 Quality parameters of aged raw leachate and RBC effluent.

Parameter	Aged raw leachate	Standard deviation	RBC effluent	Standard deviation
COD, mg/L	1,090	19	842	9
BOD_5, mg/L	39	7	17	4
Ratio of BOD_5/COD	0.04	NA	0.02	NA
Colour, TCU	1,130	7	746	13
NH_3-N, mg/L as N	455	2.0	4.9	0.4
Alkalinity, mg/L as $CaCO_3$	4,030	27	2,930	35
pH	8.30	0.01	8.70	0.01
Conductivity, mS/cm	15.1	0.1	22.3	0.1

Note:

NA: Not available.

6.2.2 Leachate oxidation

The procedure for the ozonation of the RBC effluent was the same as that described in Section 3.2.2, Chapter 3. After ozonation, all of the samples were purged with extra dry helium for 15 min to remove ozone residue.

6.2.3 Procedure for carbon mass balance

Figure 6.1 is a schematic diagram of the experimental set-up for the carbon mass balance. The extra dry oxygen gas was fed into the ozone generator, the ozonized oxygen gas was introduced into the gas-washing bottle, which was used for the ozonation of leachate samples. The ozone in the off-gas from the first gas washing bottle was absorbed using two absorption gas washing bottles with 2% potassium iodide (KI) solution, then passed through the saturated calcium hydroxide ($Ca(OH)_2$) solution at 22°C twice so that the carbon dioxide (CO_2) could be captured by the $Ca(OH)_2$ saturated solution to form the

$CaCO_3$ precipitate. The saturated $Ca(OH)_2$ solution at 22 °C had been filtered with 0.8 μm pore size filter to remove any suspended solids before it was used for capturing the CO_2 in the off-gas. The sample was ozonated for 2 hours with an inlet gas ozone concentration of 42 mg/L and at a feed gas flow rate of 3.0 L/min. All the paths of the off-gas from gas washing bottle to the fume hood were air-tight.

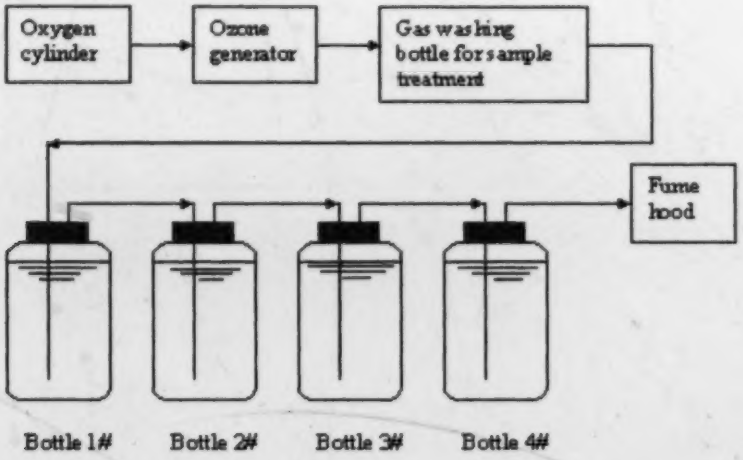

Figure 6.1 Schematic diagram of the experimental set-up for the carbon mass balance.
Bottle 1#: 4-litre bottle holding 2% KI solution;
Bottle 2#: 4-litre bottle holding 2% KI solution;
Bottle 3#: 4-litre bottle holding saturated $Ca(OH)_2$ solution (<0.8 μm, 22°C);
Bottle 4#: 4-litre bottle holding saturated $Ca(OH)_2$ solution (<0.8 μm, 22°C).

After ozonation, the leachate samples were aerated with extra dry helium for 15 min to remove any ozone residue. The total carbon (TC) and alkalinity were measured. The solutions in bottles 3# and 4# were settled for 48 h, and then the supernatants were taken out with a peristaltic pump and Tygon tubing to avoid the disturbance to the solids settled

at the bottoms of the bottles. After being concentrated, the solutions in bottles 3# and 4# were settled for one more time using the same procedure. Then the concentrated settled solids were transferred into four evaporation dishes, and dried in the oven at 103°C for 12 hours, cooled in the desiccators for 30 min, and after that, the total solid was measured. In this way, $CaCO_3$ was quantified.

6.2.4 Analytical methods

COD, BOD_5, colour, NH_3-N, alkalinity, TC were determined following the Standard Methods (American Public Health Association et al.1998). COD was analyzed in triplicate; BOD_5, colour, NH_3-N and alkalinity were measured in duplicate. TC analysis was performed with a total carbon analyzer (Shimadzu Corporation, Japan, Model: TOC-5000A) in the Limnology Laboratory of the Department of Biological Sciences of the University of Alberta.

Molecular size distribution analysis was performed with HPLC (Shimadzu Corporation, Japan) equipped with PW_{XL} guard column (Supelco/Sigma-Aldrich Canada, catalogue #: 808033, 40 mm × 6.0 mm, 12 μm particle size), $G3000PW_{XL}$ gel filtration column (Supelco/Sigma-Aldrich Canada, catalogue #: 808021, 300 mm × 7.8 mm, 6 μm particle size), and UV detector at 254 nm. The data acquisition system for the HPLC was Shimadzu Class-VP. Ten (10) mM NaCl solution filtered with 0.45 μm pore size filter as eluant, and flow rate was 0.5 mL/min. The analytical column was calibrated with polyethylene glycol (PEG) size standard solution as described in Section 3.2.4.3.4, Chapter 3.

Before injection, samples were filtered by using Millipore Millex nonsterile syringe filters with 0.45 μm pore size PVDF membrane (Fisher Scientific Canada, catalogue #:

SLHV013NL). One hundred (100) μL of filtered sample was manually injected into a 20-μL sampling loop.

6.3 Results and discussion

6.3.1 Used-ozone dose versus applied-ozone dose

Figure 6.2 depicts the relationships between the used-ozone dose and the applied-ozone dose for the ozonation of the aged raw leachate and the RBC effluent. The most important difference between the aged raw leachate and the RBC effluent was manifested in their NH_3-N difference. As NH_3-N had been removed with the air-stripping process before the RBC system, the used-ozone dose of the RBC effluent was slightly lower than that of the aged raw leachate, especially at the higher used-ozone doses.

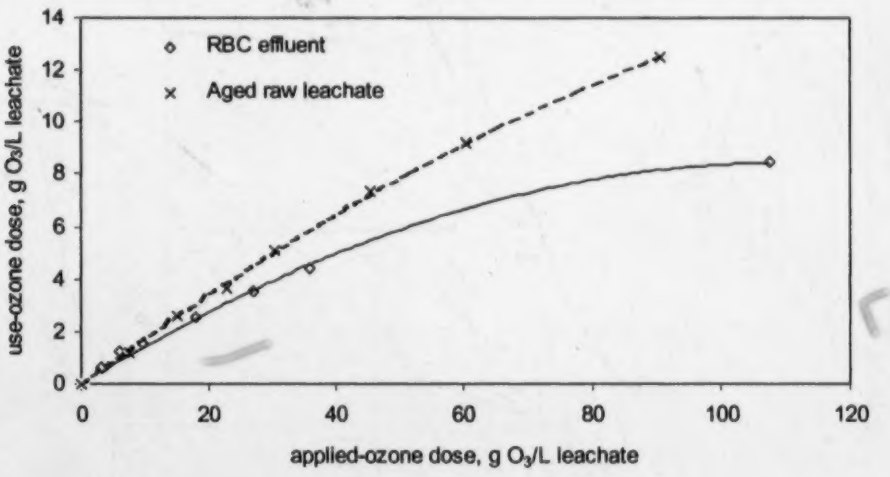

Figure 6.2 Used-ozone dose as a function of the applied-ozone dose.

6.3.2 Chemical oxygen demand (COD)

Figure 6.3 shows the effect of the used-ozone dose on the COD reduction of the

aged raw leachate and the RBC effluent. As the used-ozone dose increased up to 2.6 g O_3/L leachate for both leachates, the rate of COD reduction started to decrease. The difference, between the COD after ozonation of both leachates, was that the COD of RBC decreased faster than the COD of the aged raw leachate. This means that more COD was oxidized in the RBC effluent than in the aged raw leachate at the same used-ozone dose. This could be attributed to the RBC effluent having a very low level of NH_3-N and relatively low level of alkalinity. Therefore, the ozone utilized by the RBC effluent was used for oxidizing the COD-causing substances, thus leading to more COD reduction than that in the ozonated aged raw leachate.

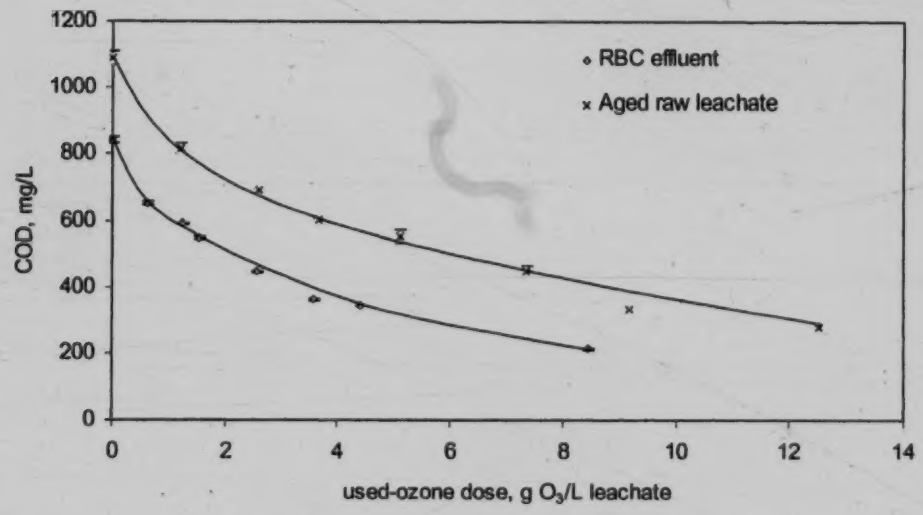

Figure 6.3 Effect of used-ozone dose on COD.

6.3.3 Five-day biochemical oxygen demand (BOD_5)

Figure 6.4 depicts the effect of the used-ozone dose on BOD_5 increase. The highest BOD_5 occurred at a used-ozone dose of 2.6 g O_3/L leachate. After the highest BOD_5 value,

the BOD_5 decreased as the used-ozone dose increased. Therefore, the optimal used-ozone dose would be 2.6 g O_3/L leachate for BOD_5 increase. This could be explained as that at the used-ozone doses up to 2.6 g O_3/L leachate, the unsaturated bonds and benzene rings of the humic substances were cleaved, and the biodegradable ozonation by-products caused the BOD_5 increase. With the increase in used-ozone dose, the biodegradable ozonation by-products were mineralized, and the BOD_5 decreased.

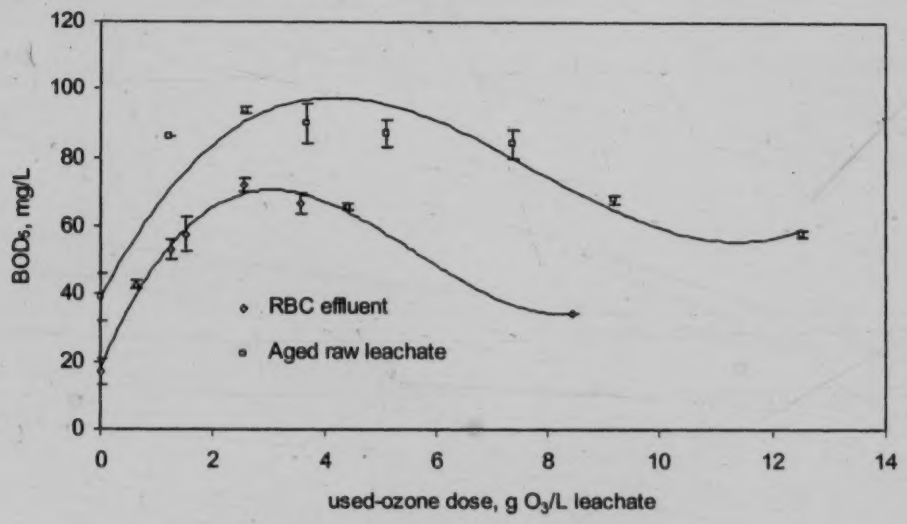

Figure 6.4 Effect of used-ozone dose on BOD_5.

The BOD_5 of both leachates had the same increase and decrease trends. The BOD_5 of RBC effluent after ozonation was always lower than that of the ozonated aged raw leachate at the same used-ozone dose. This might be caused by the following factors: First, basic and acidic chemicals as well as polymers were added to the leachate before and after RBC treatment units for accelerating the precipitation of metals and suspended solids, and air stripping of ammonia and volatile organic compounds. As a result, the conductivity of the RBC effluent (22.3 mS/cm) was higher than that of the aged raw leachate (15.1

mS/cm). The ions in the RBC effluent might act as ozone decomposition inhibitors or promoters. Therefore, the ozone reaction pathway during the treatment of the RBC effluent might have been different from that of the aged raw leachate, resulting in less biodegradable intermediate ozonation by-products and a lower BOD_5. Second, the initial COD of RBC effluent was lower than that of the aged raw leachate. Humic substances were the major COD contributors of the aged raw leachate and the RBC effluent (Chian 1977; Lecoupannec 1999). If only some functional groups of those humic substances could cause the BOD_5 increase after ozonation, the BOD_5 after ozonation would be proportional to the total amount of the humic substances (i.e., COD) of the leachate. Therefore, the lower initial COD resulted in a lower BOD_5 after ozonation.

6.3.4 Ratio of BOD_5/COD

Figure 6.5 illustrates the effect of the used-ozone dose on the ratio of BOD_5/COD improvement. The ratio of BOD_5/COD increased as the used-ozone dose increase for both leachates. After reaching their highest values, the ratios of BOD_5/COD of both leachates started to decrease as the used-ozone dose increased. Baig and Lietchi (2001) observed the similar trends during the ozonation of biologically treated pulp mill effluents. They also found that the two pulp mill effluents reached their highest values of the ratios of BOD_5/COD at different used-ozone doses since the raw materials used in these two pulp mills were not similar. At the used-ozone dose was 2.6 g O_3/L leachate, the ratio of BOD_5/COD was 0.161 and 0.136 for the RBC effluent and the aged raw leachate, respectively. This indicates that after ozonation, both leachates became biodegradable, and can be recycled to the RBC units.

Compared to the aged raw leachate ozonation, the RBC effluent had a much lower NH_3-N concentration. Without the competition for ozone caused by NH_3-N, ozone was probably able to attack the humic substances more effectively, thereby causing more cleavage of double bonds and benzene rings at lower used-ozone doses. Hence, the ratio of BOD_5/COD of RBC effluent could reach its highest value at lower used-ozone dose. After its highest value, the ratio of BOD_5/COD of RBC effluent decreased much faster than that of the aged raw leachate. Again, this was probably due to the lower NH_3-N concentration of RBC effluent.

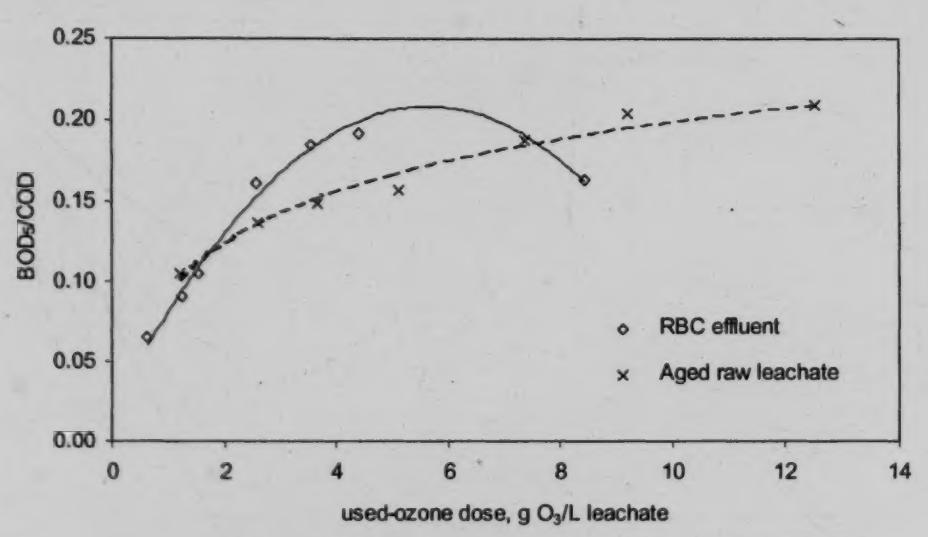

Figure 6.5 Effect of used-ozone dose on ratio of BOD_5/COD.

6.3.5 Colour

Figure 6.6 shows a colour reduction efficiency of 92% and 88% was achieved at used-ozone dose of about 2.6 g O_3/L leachate for the aged raw leachate and the RBC effluent, respectively. Meanwhile, 84% colour reduction efficiency was achieved at the used-ozone dose of 0.63 g O_3/L leachate for RBC effluent. The major fraction of the

organic substances in both leachates was humic substances (Chian 1977; Lecoupannec 1999). The colour causing functional groups in the humic substances might be quinonoid structures (Gore et al. 1962) and azo structures (Hao et al. 2000). These structures were very vulnerable to the molecular ozone attack. Therefore, the colour could be reduced effectively at low used-ozone doses.

The colour started to increase after reaching its lowest value at the used-ozone dose of 3.6 g O_3/L leachate. This might be caused by some ozonation by-products. For example, Fe^{3+} might be released from the humic substances after ozonation. Then, Fe^{3+} could form yellow iron oxide pigment [iron(III) oxide-hydroxides, FeO(OH)] at high pH (Christie 2001), and cause yellow colour.

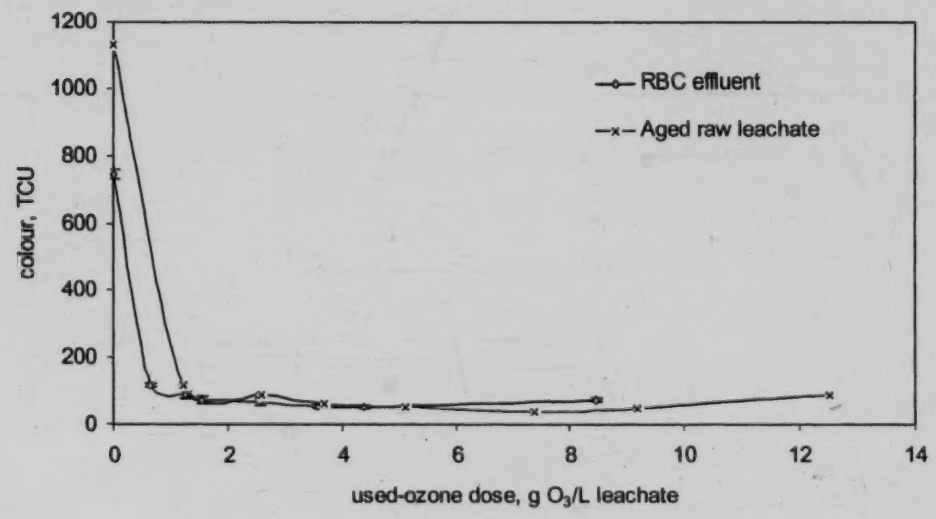

Figure 6.6 Effect of used-ozone dose on colour.

6.3.6 Alkalinity

Figure 6.7 illustrates the alkalinity changes of the aged raw leachate and the RBC effluent. For the aged raw leachate, the alkalinity decreased linearly as the used-ozone

dose increased. For the RBC effluent, the alkalinity decreased when the used-ozone dose was lower than 2.6 g O_3/L leachate. When used-ozone dose was higher than 2.6 g O_3/L leachate, the alkalinity of RBC effluent increased as the used-ozone dose increased. At the lower used-ozone dose, the alkalinity of RBC effluent decreased with the increase of used-ozone dose due to the loss of carbonate and bicarbonate alkalinity. Carbonate and bicarbonate are the inhibitors of ozonation decomposition, when the amount of these two species was reduced, ozone decomposition might become significant, and results in the formation of hydroxide ions. Therefore, the alkalinity started to increase after the lowest alkalinity value was reached at the used-ozone dose of 2.6 g O_3/L leachate.

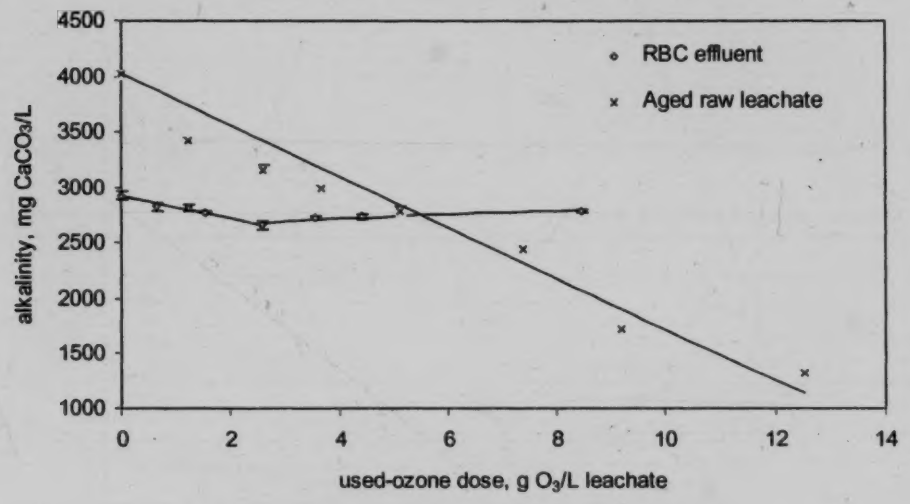

Figure 6.7 Effect of used-ozone dose on alkalinity.

6.3.7 Molecular size distribution

Figures 6.8 and 6.9 depict the molecular size distributions of the aged raw leachate and the RBC effluent before and after ozonation. It can be seen that the molecular size distributions of the aged raw leachate and the RBC effluent were not the same. Such

difference might have been caused by the high ionic strength of the RBC effluent. First, the conductivity of the RBC effluent (22.3 mS/cm) was higher than that of the aged raw leachate (15.1 mS/cm) due to the chemicals added during the physical/chemical treatments before and after RBC units. The higher ionic strength of RBC effluent could cause the humic substances (Ceccanti et al. 1989) to become smaller in molecular sizes due to (1) the detachment of the loosely connected small molecules or metal ions to the organic molecules by hydrogen bonds or Van de Waal's forces; and/or (2) the shrinkage of the molecules of humic substances. The aged raw leachate was in undisturbed ionic strength condition, which allowed the large organic compounds to stretch their molecular structures (Ceccanti et al. 1989). Therefore, four peaks were observed in the aged raw leachate, whereas, three peaks were observed in the RBC effluent.

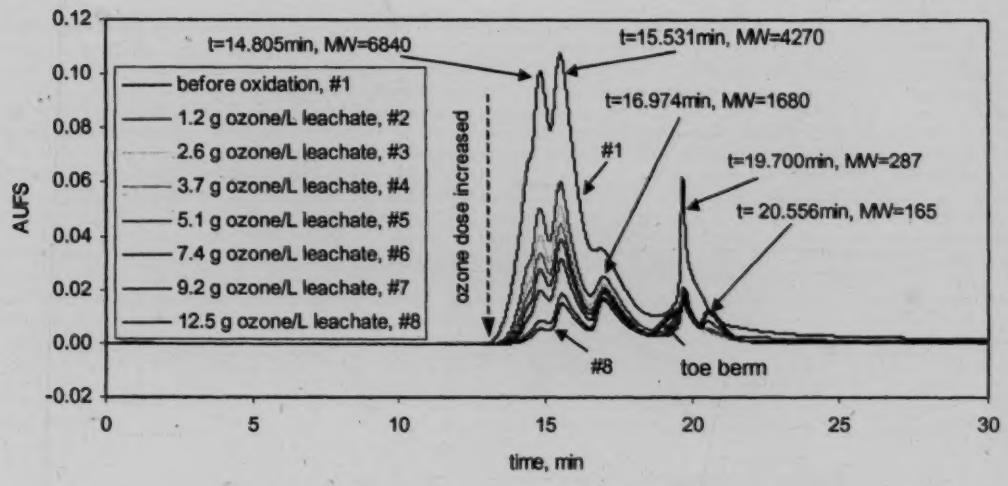

Figure 6.8 Molecular size distribution of aged raw leachate

(pH = 8.30, treatment temperature = 22°C).

For both the aged raw leachate and the RBC effluent, ozonation reduced all the peaks. For the peaks of molecular weight larger than 1,000 Dalton, the higher the used-ozone dose, the smaller the peak after ozonation. However, for the peaks with molecular weights of 287 Dalton of the aged raw leachate and 253 Dalton of the RBC effluent, an increase in the used-ozone dose did not have obvious influence on the height of those two peaks. This phenomenon might have been caused by one of the following reasons: 1) The substances of these peaks were very difficult to be oxidized; or 2) Those peaks contained some oxidation by-products of the large molecules, which had the same molecular weights. Apparently, the unchanged peaks were observed.

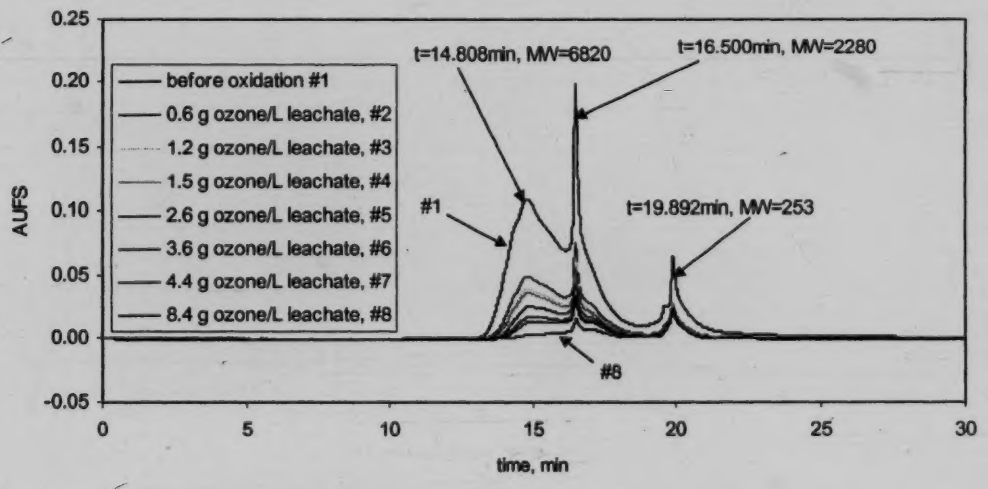

Figure 6.9 Molecular size distribution of RBC effluent

(pH = 8.70, treatment temperature = 22°C).

The oxidation by-products shown as the peak with molecular weight of 165 Dalton and shown as the toe berm on the left of the peak with molecular weight of 287 Dalton were observed for the aged raw leachate. This behaviour was not observed after oxidation

in the RBC effluent. Therefore, it seemed to show that the reduced large organic compounds in RBC effluent were oxidized to the end products, such as water and carbon dioxide.

6.3.8 Used-ozone dose, COD, BOD_5 and ratio of BOD_5/COD as functions of total peak area between molecular size distribution curve and its baseline

Figures 6.10 to 6.13 depict the relationships of the used-ozone dose, COD, BOD_5 and ratio of BOD_5/COD as functions of the total peak area, between molecular size distribution curve and baseline, for the RBC effluent and the aged raw leachate. The total peak area was obtained through the integration of UV absorbance over elution time. Therefore, the total peak area was in proportion to the total amount of organic compounds present in each sample.

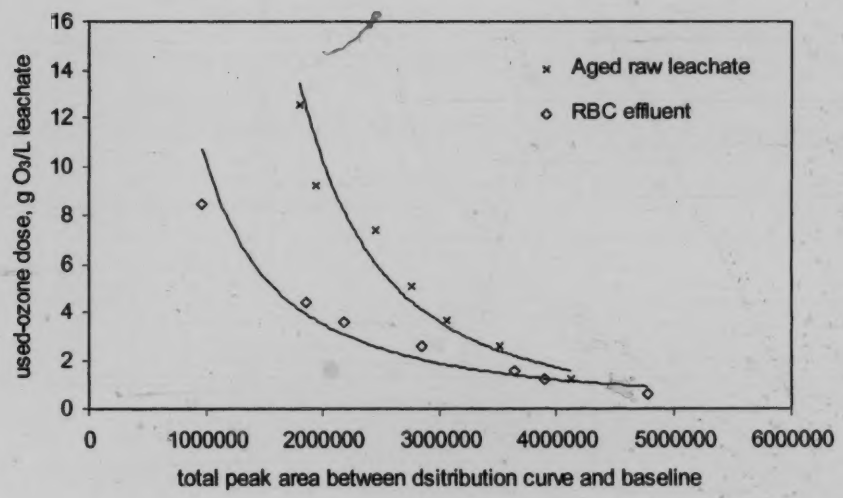

Figure 6.10 Used-ozone dose as a function of total peak area.

As shown in Figure 6.10, the total peak area for the RBC effluent was reduced more effectively than that for the aged raw leachate. This was probably because the NH_3-N concentration (4.9 mg/L as N) of the RBC effluent was only 1% of the NH_3-N concentration (455 mg/L as N) of the aged raw leachate. Without the competition of NH_3-N for ozone, the used-ozone dose was mainly utilized through the oxidation of the organic compounds.

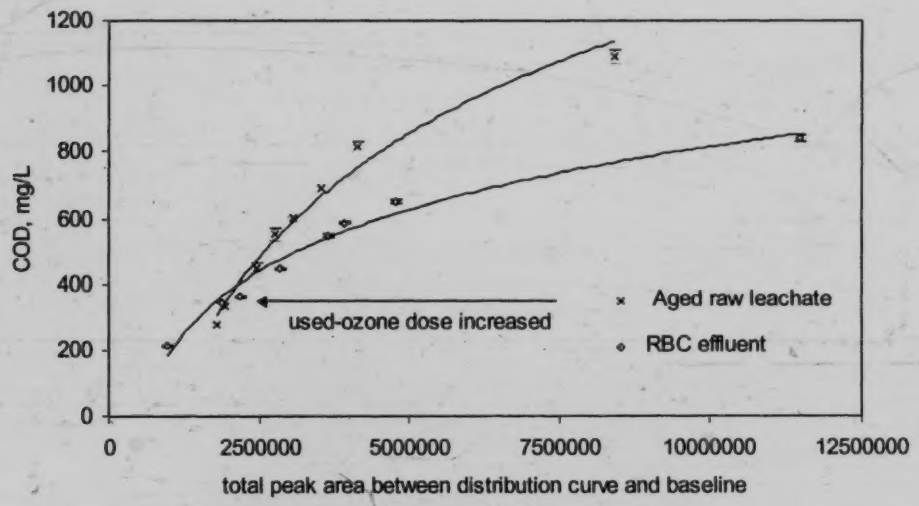

Figure 6.11 COD as a function of total peak area.

Figure 6.11 shows that the organic compounds in the RBC effluent had more UV absorbance than those in the aged raw leachate although COD before ozonation of the RBC effluent was lower than that of the aged raw leachate. As the used-ozone dose increased, COD and the total peak area of the molecular size distribution decreased. For the RBC effluent and the aged raw leachate before ozonation, the organic compounds with molecular weight larger than 300 Dalton caused 85% and 80% of the total peak area,

respectively. The amount of those compounds was reduced during the process of ozonation. This is in agreement with the results of molecular size distribution analysis.

Figure 6.12 depicts the BOD_5 of the RBC effluent and the aged raw leachate as functions of the total peak area of the molecular size distribution. Figure 6.12 suggests that the BOD_5 after ozonation was dependent on the amount of organic compounds in the sample. There are two hypotheses for such results. First, some large refractory organic compounds became biodegradable after ozonation due to molecular structure change, thus contributing to the BOD_5 increase. Second, the BOD_5 increase might have been caused by the biodegradable ozonation by-products, which may not have UV absorbance at 254 nm. To verify these hypotheses, more research is needed.

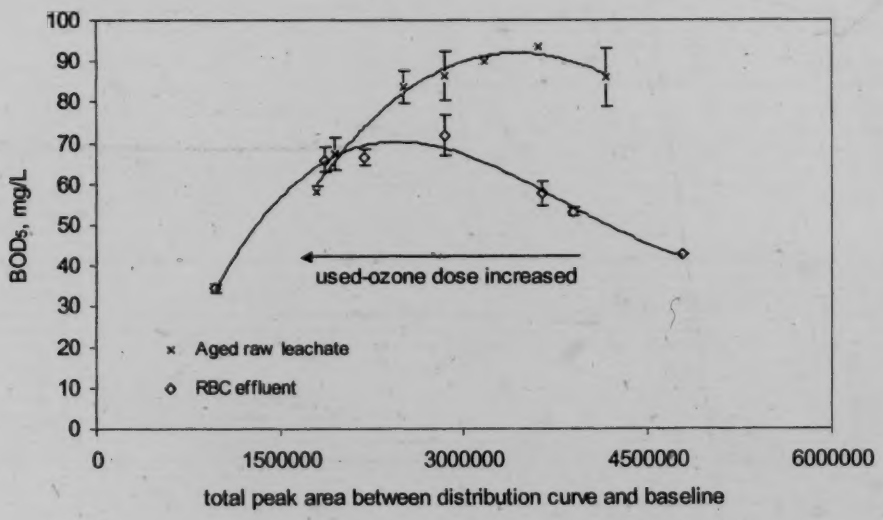

Figure 6.12 BOD_5 as a function of total peak area.

In Figure 6.13, the ratio of BOD_5/COD (i.e., biodegradability) of the RBC effluent and the aged raw leachate increased as the total peak area of the molecular size distribution was reduced. After reaching its highest value (corresponding to the used-ozone dose of 4.4

g O_3/L leachate), the ratio of BOD_5/COD of RBC effluent started to decrease while the total peak area further decreased when the used-ozone dose was larger than 4.4 g O_3/L leachate. On the other hand, the ratio of BOD_5/COD of the aged raw leachate linearly increased as the total peak area decreased.

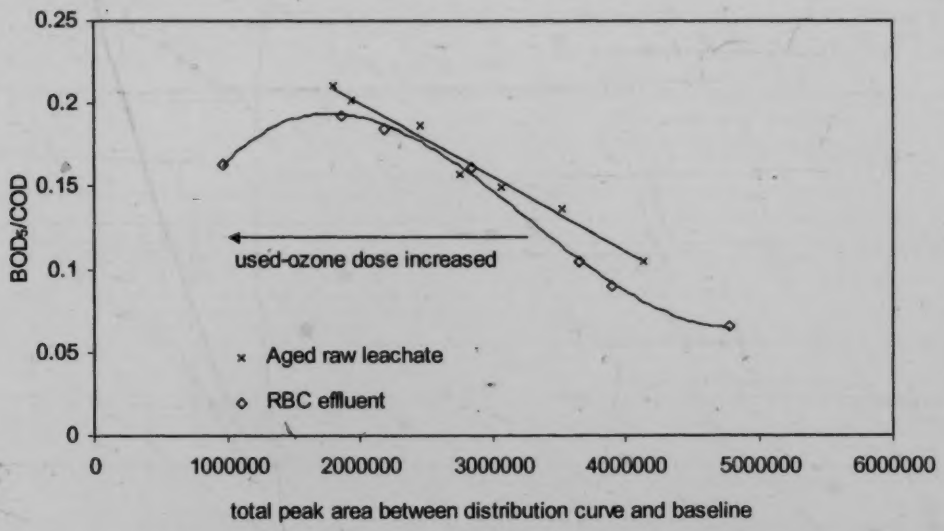

Figure 6.13 Ratio of BOD_5/COD as a function of total peak area.

The relationship between the used-ozone dose and the total peak area could be used for online ozonation process control. It takes only 30 min to obtain the total peak area of molecular size distribution; therefore, the time for feedback control can be reduced to 45 min (15 min for removing O_3 residue and 30 min for molecular size distribution analysis), and the expensive ozone can be used in an effective way. It takes three (3) hours (1 hour solution preparation and 2 hour for digestion) and five (5) days to measure COD and BOD_5, respectively; hence, the effect of ozonation on COD reduction and BOD_5 as well as ratio of BOD_5/COD improvement could be predicted in a timely fashion with these relationships.

6.3.9 Carbon mass balance for aged raw leachate oxidation with O_3 only

The concentration of $CaCO_3$, which was collected with saturated $Ca(OH)_2$ solution, was 3,340 mg /L leachate as $CaCO_3$. After ozonation, alkalinity decreased from 4,030 to 2,380 mg/L as $CaCO_3$. The lost alkalinity was 1,650 mg/L as $CaCO_3$ (4,030 – 2,380 = 1,650 mg/L as $CaCO_3$). With alkalinity of 2,380 mg/L as $CaCO_3$, used-ozone dose was (4,030 – 2,380)/232 = 7.1 g O_3/L (see Table 3.2). Using this used-ozone dose, from Table 3.2, COD after ozonation = $1{,}090 \times e^{(-0.122 \times 7.1)} = 458$ mg/L. $COD_{oxidized} = 1{,}090 - 458 = 632$ mg/L.

Based on Schulten's (1996) study, the molecular formula for a humic acid may be represented as $C_{315}H_{349}N_5O_{90}$ (molecular weight = 5,645 Dalton).

$$C_{315}H_{349}N_5O_{90} + 243.2\ O_3 = 315\ CO_2 + 174.5\ H_2O + 5\ NO_3^-$$

315×12 mg C/L 243.2×48 mg/L as COD

x 632 mg /L as COD

So, $x = 632 \times 315 \times 12/(243.2 \times 48) = 204$ mg C/L.

C	$CaCO_3$
12 mg/L as C	100 mg/L as $CaCO_3$
204 mg/L as C	y

Therefore, $y = 100 \times 204/12 = 1{,}700$ mg $CaCO_3$/L. Total $CaCO_{3\ calculated} = 1{,}700 + 1{,}650 = 3{,}350$ mg/L as $CaCO_3$. Hence, the total carbon recovery ratio is 3,340/3,350 ≈ 100%. This total carbon recovery ratio indicated that the carbon captured in the off-gas almost exactly matched the carbon loss through alkalinity reduction and organic compounds oxidation. Meanwhile, these results also demonstrated that the average

molecular weight of the humic substances used by Schulten (1996) could be applied to the humic substances in the aged raw leachate in the current study.

To verify the calculation results above, the total carbon (TC) of the samples before and after ozonation were measured. The TC before and after oxidation was 717 and 333 mg/L, respectively. The removed TC after ozonation ΔTC was 384 mg/L.

C	$CaCO_3$
12 mg/L as C	100 mg/L as $CaCO_3$
384 mg/L as C	z

Thus, $z = 100 \times 384/12 = 3{,}200$ mg/L as $CaCO_3$. Therefore, the total carbon recovery ratio is $3{,}340/3{,}200 \approx 104\%$ in terms of the removed TC. These results also showed pretty good agreement between the carbon captured in the off-gas and the total carbon removed in the aged raw leachate after ozonation. Therefore, the results obtained from carbon mass balance showed that the organic compounds in the aged raw leachate became to end products such as water, carbon dioxide, and nitrate during the ozonation process.

6.4 Conclusions

The aged raw leachate (pH = 8.30) and the RBC effluent (pH = 8.70) were ozonated using different used-ozone doses at a treatment temperature of 22 °C. The following conclusions were drawn from the results:

1. When subjected to ozonation, the COD of the aged raw leachate and the RBC effluent decreased as the used-ozone dose increased.

2. For both the aged raw leachate and RBC effluent, the highest BOD_5 occurred when the used-ozone dose was 2.6 g O_3/L leachate. This used-ozone dose is recommended for either aged raw leachate or biologically treated leachate if the purpose of ozonation treatment is to increase the leachate biodegradability.
3. At the used-ozone dose of 2.6 g O_3/L leachate, the ratio of BOD_5/COD after ozonation increased from 0.02 to 0.161 for the RBC effluent and from 0.04 to 0.136 for the aged raw leachate. The results show that the RBC effluent and the aged raw leachate after ozonation became biodegradable, and can be recycled into RBC units.
4. Colour was reduced by 92% and 88% for the aged raw leachate and RBC effluent, respectively, at a used-ozone dose of 2.6 g O_3/L leachate. For RBC effluent, 84% colour removal efficiency was even achieved at a used-ozone dose of 0.63 g O_3/L leachate.
5. Alkalinity of the aged raw leachate decreased linearly as the ozonation continued. Meanwhile, the alkalinity of the RBC effluent decreased when the used-ozone dose was smaller than 2.6 g O_3/L leachate, and then increased as the used-ozone dose increased.
6. The molecular size distributions showed that the peaks of large molecules decreased as the used-ozone dose increased for both leachates. New peaks with small molecular weights after ozonation were observed for the aged raw leachate, and not observed for the RBC effluent. The molecular size distributions of the RBC effluent were quite different from those of the aged raw leachate possibly due to the change in the ionic strength of the RBC effluent as a result of the physical/chemical treatment processes before and after RBC units.

7. The relationships of the used-ozone dose, COD, BOD_5 and ratio of BOD_5/COD as functions of the total peak area between the molecular size distribution curve and its baseline for both the aged raw leachate and the RBC effluent may be used for ozonation process control as well as the treatment efficiency prediction for COD, BOD_5 and ratio of BOD_5/COD.
8. The carbon mass balance of the aged raw leachate showed good agreement between the carbon captured in the off-gas and the calculated carbon loss due to the alkalinity reduction and the organic compounds oxidation, as well as between the carbon captured in the off-gas and the total carbon removed of the leachate after ozonation.

6.5 References

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CHAPTER 7 GENERAL CONCLUSIONS AND RECOMMENDATIONS

7.1 General overview

The aged raw landfill leachate as well as the biologically treated landfill leachate is one category of wastewaters that are very difficult to deal with because of the low ratio of BOD_5/COD and the complicated constituents. Therefore, how to treat this kind of wastewater still draws much research attention. Although the advanced oxidation of aged raw or biologically treated landfill leachate has been extensively investigated in the past decade as mentioned in Chapters 2, 3 and 5, most of the investigations were focused on the treatment efficiency for the reduction of COD, colour, TOC, and DOC and/or the increase of BOD_5. The following areas are still not well understood: (1) The ammonia nitrogen and alkalinity change during the oxidation processes; (2) The by-products that are produced when a complex matrix like landfill leachate is subjected to ozonation; (3) For the H_2O_2/UV process, which is the most important factor among leachate pH, H_2O_2 dose and UV fluence, for the reduction of COD and colour and the improvement of biodegradability; (4) Whether or not H_2O_2 plays an important role in the combined oxidation processes of O_3/H_2O_2 and H_2O_2/UV; (5) No information available with regard to the molecular size distribution of the landfill leachate after oxidation with H_2O_2-related processes; (6) The residue of H_2O_2 in leachate samples was usually removed with either Bovine liver catalase or $Na_2S_2O_3$, both of which have a severe influence on the molecular size distribution analysis.

The major objectives of the current research mainly focused on the above issues.

7.2 Conclusions

Based on the experimental and theoretical studies in this research, the following conclusions were drawn:

7.2.1 Aged raw leachate: O_3 only, O_3/H_2O_2, and H_2O_2/UV

1. Compared to the O_3 only process, the effect of addition of H_2O_2 to aged raw leachate immediately before ozonation was not statistically significant (at a 95% confidence level) to the reduction of COD, colour, NH_3-N and alkalinity, or the increase of the ratio of BOD_5/COD.
2. The regression models of the COD, ratio of BOD_5/COD, NH_3-N and alkalinity as functions of the used-ozone dose were developed for O_3 only and O_3/H_2O_2 separately, and the pooled models with regard to the above parameters were also developed.
3. The molecular size distribution analyses demonstrated that the addition of H_2O_2 at the dose of 0.63 g H_2O_2/L leachate slightly enhanced the reduction of the peaks with molecular weight higher than 1,680 Dalton at lower used-ozone doses. This finding was in agreement with the COD results. The peaks with molecular weight higher than 1,680 Dalton became smaller as the used-ozone dose increased. Nevertheless, the peak with molecular weight of 287 Dalton did not change significantly. Meanwhile, the new peaks after oxidation at 20.556 min (molecular weight 165 Dalton) and the toe berm on the left of the peak at 19.700 min (molecular weight 287 Dalton) increased as the used-ozone dose increased. There was no obvious correlation observed between the oxidation by-product formation and the BOD_5 increase after oxidation.

4. The carbon mass balance on the aged raw leachate oxidized with O_3 only showed very good agreement between the carbon captured in the off-gas during ozonation and the calculated carbon loss in the alkalinity reduction and the organic compound oxidation. There was also pretty good agreement between the carbon captured in the off-gas of ozonation and the total carbon loss of the leachate before and after ozonation as well.
5. When the aged raw leachate was oxidized with the H_2O_2/UV process, a 2^3 factorial experiment demonstrated that the important factors for COD reduction were UV fluence, H_2O_2 dose, and leachate pH. UV fluence was the significant factor for BOD_5 improvement. The important factors for colour reduction were UV fluence and H_2O_2 dose.
6. Suspended particles in the aged raw leachate samples hindered the reduction of the large molecule peaks of the molecular size distributions and the COD reduction of the H_2O_2/UV process.

7.2.2 Aged raw leachate: Mass distribution profiles of COD, BOD_5, colour, and metals

1. After membrane fractionation of the aged raw leachate, Co, Cr, Cu, Fe, Mo, Ni, Pb, Sb, Sn, Ti, and Zn were enriched in the samples of 0.45 μm to 10,000 Dalton and 10,000 to 5,000 Dalton; Ag, Al, As, Cd, and Hg were enriched in the sample of 0.45 μm to 10,000 Dalton; V was enriched in the sample of 5,000 to 1,000 Dalton; and Bi was enriched in the sample of <1,000 Dalton.
2. The major COD and BOD_5 contributors were organic compounds with molecular weight less than 10,000 Dalton, while the major colour contributors were the organic compounds with molecular weight larger than 1,000 Dalton.

7.2.3 Fractionated aged raw leachates: O_3 only and O_3/H_2O_2

1. The addition of H_2O_2 had less effect on the COD reduction for the samples of 10,000 to 5,000 Dalton and 5,000 to 1,000 Dalton than the samples of 0.45 μm to 10,000 Dalton and <1,000 Dalton.
2. More BOD_5 increase occurred for the two fractions of 10,000 to 5,000 Dalton and 5,000 to 1,000 Dalton.
3. Colour removal efficiency for the samples of 0.45 μm to 10,000 Dalton; 10,000 to 5,000 Dalton; and 5,000 to 1,000 Dalton was above 87%, but for the sample <1,000 Dalton, colour removal efficiency was 69% for O_3/H_2O_2 and 51% for O_3 only.
4. The addition of H_2O_2 enhanced the reduction of the peaks with molecular weights larger than 1,000 Dalton. This effect of the H_2O_2 addition was obvious for the samples of aged raw leachate, 0.45 μm to 10,000 Dalton and <1,000 Dalton. Meanwhile, this effect was small for the samples of 10,000 to 5,000 Dalton and 5,000 to 1,000 Dalton.
5. There were no new peaks observed after oxidation with O_3/H_2O_2 for all the samples. After oxidation with O_3 only, oxidation by-products with molecular weight less than 200 Dalton were observed in the samples of 10,000 to 5,000 Dalton; 5,000 to 1,000 Dalton; and <1,000 Dalton. No correlation between the new peak formation and BOD_5 increase was found. Conversely, BOD_5 of each sample after oxidation with O_3 only was the logarithmic function of its total peak area between the molecular size distribution curve and its baseline.

7.2.4 Fractionated aged raw leachates: H_2O_2/UV at pH = 4.50

1. The COD reduction of the aged raw leachate and the fractionated aged raw

leachates varied from 74 to 279 mg/L.

2. Compared to the aged raw leachate (containing particles), the BOD_5 of fractionated aged raw leachates (particle-free) increased more.
3. H_2O_2/UV treatment effectively reduced colour for the fractionated aged raw leachates, but it was less effective for the colour reduction for the aged raw leachate.
4. Molecular size distribution analysis demonstrated that no new peaks were observed for the samples except that of 0.45 μm to 10,000 Dalton. For the sample of 0.45 μm to 10,000 Dalton, the peak with molecular weight of 1,720 Dalton may be either the oxidation by-products or the leftover of the organic compounds that could not be oxidized by H_2O_2/UV process.

7.2.5 RBC effluent: O_3 only

1. The highest BOD_5 values appeared when the used-ozone dose was 2.6 g O_3/L leachate. This used-ozone dose is recommended for the oxidation of biologically treated leachate if the ozonation purpose is to increase the leachate biodegradability.
2. At the used-ozone dose of 2.6 g O_3/L leachate, COD removal efficiency was 47%, and the ratio of BOD_5/COD was 0.16, which indicates that the ozonated RBC effluent became biodegradable and was suitable for being recycled to the RBC units.
3. Colour was reduced by 88% for the RBC effluent at a used-ozone dose of 2.6 g O_3/L RBC leachate. 84% colour reduction was achieved at a used-ozone dose of 0.63 g O_3/L leachate.

4. Alkalinity of the RBC effluent decreased when the used-ozone dose was less than 2.6 g O_3/L leachate, and then started to increase.
5. The molecular size distributions showed that the peaks of large molecules decreased as the ozonation continued for the RBC effluent. No new peaks were observed after ozonation. The molecular size distributions of the RBC effluent were quite different from those of the aged raw leachate since the ionic strength of the RBC effluent has been changed as a result of the physical/chemical and the biological treatments.
6. The relationships between the used-ozone dose, COD, BOD_5 and ratio of BOD_5/COD as functions of the total peak area between the molecular size distribution curve and its baseline were established for both the aged raw leachate and the RBC effluent.

7.3 Recommendations

In this research project, the aged raw leachate as well as the membrane fractionated aged raw leachates were oxidized with O_3 only, O_3/H_2O_2 and H_2O_2/UV. Meanwhile, the RBC effluent was oxidized with O_3 only. Based on the results and the drawn conclusions, the following recommendations need to be addressed for future research:

1. The applicability of the regression models of COD, BOD_5/COD, NH_3-N and alkalinity as functions of the used-ozone dose needs to be verified with continuous-flow ozone bubble column and aged raw leachate as well as biologically treated leachate from different landfill sites. After the verification has been done, these models may be used to predict the treatment efficiency of the leachate ozonation.

2. The fundamentals of the BOD_5 improvement of landfill leachate after advanced oxidation need to be further investigated. In addition to molecular size distribution analysis, nuclear magnetic resonance (NMR) and infrared ray (IR) techniques can be used for analyzing the changes in molecular structures and functional groups before and after advanced oxidation.
3. Relationships between the used-ozone dose, COD, BOD_5 and ratio of BOD_5/COD as functions of the total peak area between the molecular size distribution curve and its baseline need to be further verified with continuous-flow ozone bubble column reactor at the bench- or pilot-scale. These regression models may be applied to control the ozone dosing as well as to predict treatment efficiency of COD, BOD_5 and BOD_5/COD of the ozone bubble column reactor.

APPENDICES

Appendix 3.1 Statistical analysis of COD of O_3 only and O_3/H_2O_2 versus used-ozone dose

The data were given in Table A3.1.

Table A3.2 Statistical analysis for COD of O_3 only and O_3/H_2O_2 (Zar 1999)

O_3						O_3/H_2O_2					
x_1	x_1^2	y_{10}	y_1	y_1^2	x_1y_1	x_2	x_2^2	y_{20}	y_2	y_2^2	x_2y_2
12.52	156.7106	277.4	-1.369	1.8750	-17.1414	13.80	190.4343	239.0	-1.518	2.3055	-20.9534
9.19	84.4893	333.5	-1.185	1.4045	-10.8934	10.26	105.2155	330.4	-1.195	1.4269	-12.2530
7.37	54.3020	447.8	-0.890	0.7928	-6.5614	7.81	60.9507	361.6	-1.104	1.2195	-8.6215
5.11	26.1349	552.7	-0.680	0.4623	-3.4760	5.98	35.7774	475.8	-0.830	0.6887	-4.9637
3.67	13.5035	603.6	-0.592	0.3503	-2.1749	5.08	25.8315	524.7	-0.732	0.5359	-3.7205
2.60	6.7533	689.9	-0.458	0.2100	-1.1908	3.57	12.7558	581.8	-0.629	0.3953	-2.2455
1.21	1.4656	816.6	-0.290	0.0839	-0.3506	1.82	3.3296	672.2	-0.484	0.2345	-0.8837
Σ	343.3591			5.1787	-41.7885	Σ	434.2949			6.8063	-53.6413
		$b_1 = -0.122$						$b_2 = -0.124$			
		$n = 7$						$n = 7$			
		$X_{1a} = 5.95$						$X_{2a} = 6.90$			
		$Y_{1a} = -0.781$						$Y_{2a} = -0.927$			

Notes:

b_1 = regression slope for O_3 only;

x_1 = used-ozone dose for O_3 only, g O_3/L leachate;

y_{10} = COD, mg/L for O_3 only;

$y_1 = \ln(COD/COD_0)$ for O_3 only;

X_1a = average value of used-ozone dose for O_3 only, g O_3/L leachate;

Y_1a = average value of $\ln(COD/COD_0)$ for O_3 only;

b_2 = regression slope for O_3/H_2O_2;

x_2 = used-ozone dose for O_3/H_2O_2, g O_3/L leachate;

y_{20} = COD, mg/L for O_3/H_2O_2;

$y_2 = \ln(COD/COD_0)$ for O_3/H_2O_2;

X_2a = average value of used-ozone dose for O_3/H_2O_2, g O_3/L leachate;

Y_2a = average value of $\ln(COD/COD_0)$ for O_3/H_2O_2, g O_3/L leachate.

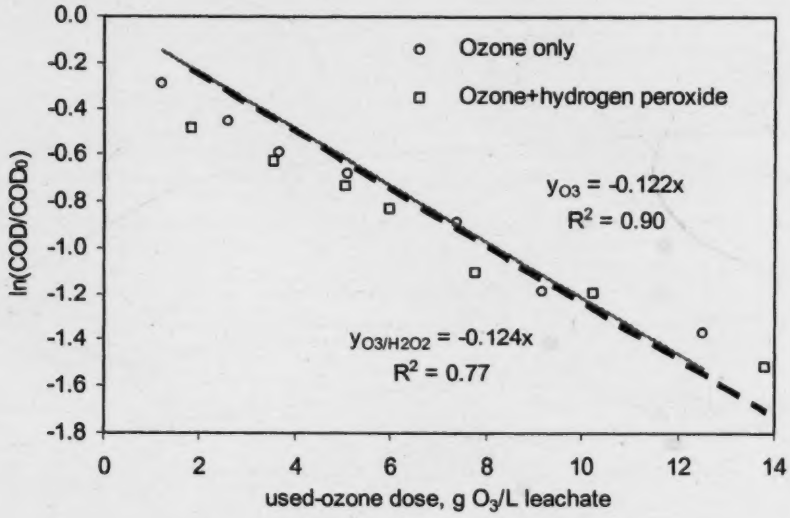

Figure A3.1 Plot of linearized COD against used-ozone dose.

Testing for the difference between the regression slopes of COD versus used-ozone dose of O_3 only and O_3/H_2O_2

Hypothesis

H_0: $\beta_1 = \beta_2$, the difference between the regression slopes of COD versus used-ozone dose of O_3 only and O_3/H_2O_2 was not statistically significant.

H_A: $\beta_1 \neq \beta_2$, the difference between the regression slopes of COD versus used-ozone dose of O_3 only and O_3/H_2O_2 was statistically significant.

Residual $SS_1 = \sum y_1^2 - (\sum x_1 y_1)^2 / \sum x_1^2$

$= 5.1787-(-41.7885)^2/343.3591$

$=0.09283$

Residual $DF_1 = 7 - 2 = 5$

Residual $SS_2 = \sum y_2^2 - (\sum x_2 y_2)^2/\sum x_2^2$

$= 6.8063 - (-53.6413)^2/434.2949$

$= 0.1809$

Residual $DF_2 = 7 - 2 = 5$

$(s^2_{Y \bullet X})_p = (0.09283 + 0.1809)/(5 + 5) = 0.02737$

$s_{b1-b2} = (0.02737/343.3591+0.02737/434.2949)^{1/2} = 0.01195$

$t = (-0.0972-(-0.0876))/0.01195 = -0.8033$

$\nu = 5 + 5 = 10$

Reject H_0 if $|t| \geq t_{\alpha(2),\nu}$

$t_{0.05(2),10} = 2.228 > |t| = 0.8033$. Therefore, H_0: $\beta_1 = \beta_2$ was not rejected, $P > 0.5$.

In conclusion, the regression of $\ln(COD/COD_0)$ after O_3 only against used-ozone dose and the regression of $\ln(COD/COD_0)$ after O_3/H_2O_2 against used-ozone dose statistically had the same slope. Hence, the addition of H_2O_2 at 0.63 g H_2O_2/L leachate did not significantly enhance the COD reduction.

Reference

Zar, J. H.1999. *Biostatistical Analysis* (4th Ed.). Prentice-Hall Canada Inc., Toronto, Canada. 663p.

Appendix 3.2 Statistical analysis of BOD_5/COD of O_3 only and O_3/H_2O_2 versus ln(used-ozone dose)

The data are given in Table A3.2

Table A3.2 Statistical analysis for BOD_5/COD of O_3 only and O_3/H_2O_2 (Zar 1999)

O_3					O_3/H_2O_2				
x_1	x_1^2	y_1	y_1^2	x_1y_1	x_2	x_2^2	y_2	y_2^2	x_2y_2
2.53	6.39	0.211	0.044	0.532	2.62	6.89	0.193	0.037	0.506
2.22	4.92	0.202	0.041	0.449	2.33	5.42	0.193	0.037	0.450
2.00	3.99	0.187	0.035	0.373	2.06	4.22	0.195	0.038	0.401
1.63	2.66	0.157	0.025	0.256	1.79	3.20	0.165	0.027	0.295
1.30	1.69	0.149	0.022	0.194	1.63	2.64	0.151	0.023	0.246
0.96	.91	0.136	0.018	0.130	1.27	1.62	0.140	0.020	0.179
0.19	0.04	0.105	0.011	0.020	0.60	0.36	0.117	0.014	0.070
1.55		0.164			1.76		0.165		
sum	20.60		0.197	1.954	sum	24.36		0.196	2.148
		$b_1 = 0.047$					$b_2 = 0.043$		
		$a_1 = 0.092$					$a_2 = 0.089$		
		$X_1a = 1.55$					$X_2a = 1.76$		
		$Y_1a = 0.164$					$Y_2a = 0.165$		

Notes:

b_1 = regression slope for O_3 only;

a_1 = regression elevation for O_3 only;

x_1 = ln (used-ozone dose) for O_3 only;

y_1 = BOD_5/COD for O_3 only;

X_1a = average value of ln (used-ozone dose) for O_3 only;

Y_1a = average value of BOD_5/COD for O_3 only;

b_2 = regression slope for O_3/H_2O_2;

a_2 = regression elevation for O_3/H_2O_2;

x_2 = ln (used-ozone dose) for O_3/H_2O_2;

y_2 = BOD_5/COD for O_3/H_2O_2.

X_2a = average value of ln (used-ozone dose) for O_3/H_2O_2;

Y_2a = average value of BOD_5/COD for O_3/H_2O_2.

Testing for the difference between the regression slopes of BOD_5/COD versus ln (used-ozone dose)

Hypothesis

H_0: $\beta_1 = \beta_2$, the difference between the regression slopes of BOD_5/COD versus ln (used-ozone dose) of O_3 only and O_3/H_2O_2 was not statistically significant.

H_A: $\beta_1 \neq \beta_2$, the difference between the regression slopes of BOD_5/COD versus ln (used-ozone dose) of O_3 only and O_3/H_2O_2 was statistically significant.

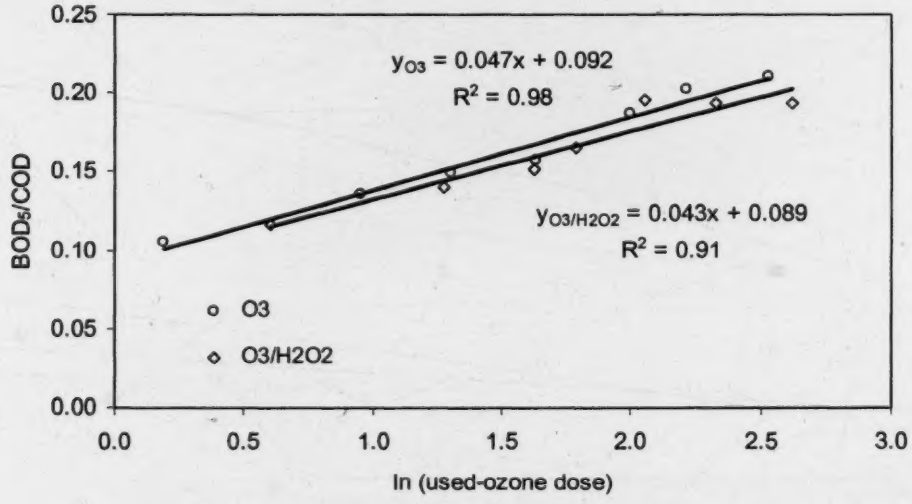

Figure A3.2 Plot of BOD_5/COD versus ln(used-ozone dose)

Residual $SS_1 = \sum y_1^2 - (\sum x_1 y_1)^2 / \sum x_1^2$

$= 0.197 - (1.954)^2/20.60$

$= 0.012$

Residual $DF_1 = 7 - 2 = 5$

Residual $SS_2 = \sum y_2^2 - (\sum x_2 y_2)^2/\sum x_2^2$

$= 0.196 - (2.148)^2/24.36$

$= 0.007$

Residual $DF_2 = 7 - 2 = 5$

$(s^2_{Y \bullet X})_p = (0.012 + 0.007)/(5 + 5) = 0.0019$

$s_{b1-b2} = (0.0019/20.60 + 0.0019/24.36)^{1/2} = 0.018$

$t = (0.047 - 0.043)/0.018 = 0.222$

$\nu = 5 + 5 = 10$

Reject H_0 if $|t| \geq t_{\alpha(2),\nu}$

$t_{0.05(2),10} = 2.228 > |t| = 0.222$. Therefore, H_0: $\beta_1 = \beta_2$ was not rejected, $P > 0.5$. That means the regression slopes of BOD_5/COD versus ln(used-ozone dose) for O_3 only and O_3/H_2O_2 were the same.

Testing for the difference between the regression elevations of BOD_5/COD versus ln(used-ozone dose) of O_3 only and O_3/H_2O_2

Hypothesis

H_0: The regression elevations of BOD_5/COD versus ln(used-ozone dose) of O_3 only and O_3/H_2O_2 were same.

H_A: The regression elevations of BOD_5/COD versus ln(used-ozone dose) of O_3 only and O_3/H_2O_2 were not same.

$A_c = 20.60 + 24.36 = 44.96$

$B_c = 1.954 + 2.148 = 4.102$

$C_c = 0.197 + 0.196 = 0.393$

$b_c = 4.102/44.96 = 0.091$

$SS_c = 0.393 - (4.102)^2/44.96 = 0.019$

$DF_c = 7 + 7 - 3 = 11$

$(s^2_{Y \bullet X})_c = 0.019/11 = 0.0017$

$t = [(0.164 - 0.165) - 0.091(1.55 - 1.76)]/$

$\{0.0017[1/7+1/7+(1.55-1.76)^2/44.96]\}^{1/2}$

$= 0.018/0.022$

$= 0.818$

$t_{0.05(2),11} = 2.201 > |t| = 0.818$, $P > 0.44$. Therefore, H_0 was true.

In conclusion, the regression of BOD_5/COD versus ln(used-ozone dose) after O_3 only and the regression of BOD_5/COD versus ln(used-ozone dose) after O_3/H_2O_2 statistically had the same slope and the same elevation. Hence, the addition of H_2O_2 at 0.63 g H_2O_2/L leachate did not significantly affect the BOD_5/COD change in the processes of O_3 only and O_3/H_2O_2.

Reference

Zar, J. H. 1999. *Biostatistical Analysis* (4th Ed.). Prentice-Hall Canada Inc., Toronto, Canada. 663p.

Appendix 3.3 Statistical analysis of alkalinities of O_3 only and O_3/H_2O_2 versus used-ozone dose

The data were given in Table A3.3.

Table A3.3 Statistical analysis for alkalinity of O_3 only and O_3/H_2O_2 (Zar 1999)

O_3					O_3/H_2O_2				
x_1	x_1^2	y_1	y_1^2	x_1y_1	x_2	x_2^2	y_2	y_2^2	x_2y_2
0.00	0	4025	16200625	0	0.0	0.0000	4025	16200625	0.0
12.52	156.71	1333	1777172	16688.4	13.80	190.43	1290	1664358	17803.1
9.19	84.49	1727	2981458	15871.4	10.26	105.22	2008	4033269	20600.1
7.37	54.30	2450	6004344	18056.8	7.81	60.95	2474	6119686	19313.2
5.11	26.13	2793	7801827	14279.4	5.98	35.78	3126	9768750	18694.9
3.67	13.50	2996	8977904	11010.6	5.08	25.83	3378	11412235	17169.6
2.60	6.75	3161	9994237	8215.5	3.57	12.76	3724	13868176	13300.4
1.21	1.47	3428	11751098	4149.9	1.82	3.33	3897	15185830	7110.8
5.95		2556			6.90		2842		
sum	343.36		49288039	88271.9	sum	434.29		62052304	113992
		$b_1 = -232$					$b_2 = 185$		
		$a_1 = 4030$					$a_2 = 4030$		
		$X_1a = 5.95$					$X_2a = 6.90$		
		$Y_1a = 2556$					$Y_2a = 2842$		

Note:

b_1 = regression slope for O_3 only;

a_1 = regression elevation for O_3 only;

x_1 = used-ozone dose for O_3 only, g O_3/L leachate;

y_1 = alkalinity for O_3 only, mg $CaCO_3$/L;

X_1a = average value of used-ozone dose for O_3 only, g O_3/L leachate;

Y_1a = average value of alkalinity for O_3 only, mg $CaCO_3$/L;

b_2 = regression slope for O_3/H_2O_2;

a_2 = regression elevation for O_3/H_2O_2;

x_2 = used-ozone dose for O_3/H_2O_2, g O_3/L leachate;

y_2 = alkalinity for O_3/H_2O_2, mg $CaCO_3$/L;

X_2a = average value of used-ozone dose for O_3/H_2O_2, g O_3/L leachate;

Y_2a = average value of alkalinity for O_3/H_2O_2, mg $CaCO_3$/L.

Testing for the difference between the regression slopes of alkalinity versus used-ozone dose of O_3 only and O_3/H_2O_2

Hypothesis

H_0: $\beta_1 = \beta_2$, the difference between the regression slopes of alkalinities versus used-ozone dose of O_3 only and O_3/H_2O_2 was not statistically significant.

H_A: $\beta_1 \neq \beta_2$, the difference between the regression slopes of alkalinities versus used-ozone dose of O_3 only and O_3/H_2O_2 was statistically significant.

Residual $SS_1 = \sum y_1^2 - (\sum x_1 y_1)^2/\sum x_1^2$

$= 49288039 - (88271.9)^2/343.36$

$= 26594865$

Residual $DF_1 = 7 - 2 = 5$

Residual $SS_2 = \sum y_2^2 - (\sum x_2 y_2)^2/\sum x_2^2$

$= 62052304 - (113992)^2/434.29$

$= 32131799$

Residual $DF_2 = 7 - 2 = 5$

$(s^2_{Y \bullet X})_p = (26594865 + 32131799)/(5 + 5) = 5872666$

$s_{b1-b2} = (5872666/343.36 + 5872666/434.29)^{1/2} = 175.0$

$t = (-231.5 - (-185.4))/175.0 = -0.2634$

$\nu = 5 + 5 = 10$

Reject H_0 if $|t| \geq t_{\alpha(2),\nu}$

$t_{0.05(2),10} = 2.228 > |t| = 0.2634$. Therefore, H_0: $\beta_1 = \beta_2$ was not rejected, $P > 0.5$.

Testing for the difference between the regression elevations of alkalinity versus used-ozone dose of O_3 only and O_3/H_2O_2

Hypothesis

H_0: The regression elevations of alkalinity versus used-ozone dose of O_3 only and O_3/H_2O_2 are same.

H_A: The regression elevations of alkalinity versus used-ozone dose of O_3 only and O_3/H_2O_2 are not same.

$A_c = 343.36 + 434.29 = 777.65$

$B_c = (88271.9) + (113992) = 202263.9$

$C_c = 49288039 + 62052304 = 11134034$

$b_c = 202263.9/777.654 = 260.1$

$SS_c = 111340343 - (202263.9)^2/777.65 = 58732248$

$DF_c = 7 + 7 - 3 = 11$

$(s^2_{Y \bullet X})_c = 58732248/11 = 5339295$

$t = [(2556-2842) - 260.1(5.95-6.90)]/$

$\{5339295[1/7+1/7+(5.95-6.90)^2/777.65]\}^{1/2}$

$= -38.91/1237.6$

$= -0.0314$

$t_{0.05(2),11} = 2.201 > |t| = 0.0314$, $P > 0.5$. Therefore, H_0 was true.

In conclusion, the regression of alkalinity after O_3 only against used-ozone dose and the regression of alkalinity after O_3/H_2O_2 against used-ozone dose statistically had the same slope and the same elevation. Hence, the addition of H_2O_2 at 0.63 g H_2O_2/L leachate did not significantly affect the alkalinity change in the processes of O_3 only and O_3/H_2O_2.

Reference

Zar, J. H. 1999. *Biostatistical Analysis* (4th Ed.) Prentice-Hall Canada Inc., Toronto, Canada. 663p.